Highly Selective Lithium–Amine Reducing Systems. The Selective Reduction of Aromatic Compounds by Lithium in Mixed Amine Solvents[1a]

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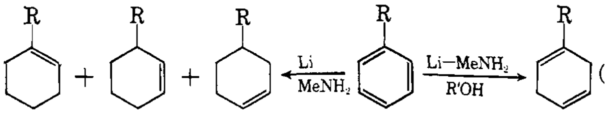
Changes in the primary amines normally employed as solvents for reducing aromatic compounds with lithium have a marked effect upon product composition. Systematic variation of the solvent from methyl- to ethyl- to *n*-propylamine caused a gradual increase in the percentage of 1-alkyl cyclohexenes obtained from the reduction of alkyl benzenes. The effect was even more dramatic when the primary amine was diluted with a secondary amine like dimethylamine or morpholine. Addition of these secondary amines not only provided much greater selectivity in the reduction, but at the same time lowered the over-all volatility of the solvent system, affording greater ease of handling. The equilibrium isomer distributions of methyl- and *t*-butylcyclohexene were determined. From the results it is deemed unlikely that the monoolefins produced in these reductions are isomerized to any appreciable extent under the conditions of the reaction. Rather, the final product composition seems determined by the nature and concentrations of the cyclohexadiene precursors.

In the previous paper in this series,[1b] it was shown that the addition of alcohol to a solution of lithium in methylamine has a profound effect on the reducing properties of this system. Normally, aromatic hydrocarbons are reduced selectively to monoolefins (tetrahydro products) by the lithium–amine reagent.[2] In the presence of an alcohol, however, two equivalents of lithium (based on aromatic) dissolved in methylamine will reduce aromatic compounds quite selectively to the dihydro stage.



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When carried out under these conditions the reaction resembles the celebrated Birch reduction.

In this paper we report the effect of variations in the amine solvents on the course of the reduction whereby some light is thereby cast on the mechanism of these reductions.

As was reported earlier,[3] certain low molecular weight aliphatic amines are effective solvents in the reduction of aromatic hydrocarbons by lithium. In order to assess the relative merits of various amine solvents, a detailed study was made of the reduction of toluene, isopropyl- and *t*-butylbenzene in methyl-, ethyl-, and *n*-propylamine. All reactions were carried out at −7°, the boiling point of methylamine. The results of these experiments are listed in Table I. Two things are immediately apparent from the data. (1) The ratio of the 1-olefin relative to the 3- and 4-olefin increases as the alkyl group of the amine becomes larger. (2) The rate of reduction of the hydrocarbons decreases (as evidenced by the recovery of aromatic) as the molecular weight of the amine increases. Particularly in the case of *n*-propylamine, the direct reaction of the metal with the solvent to form hydrogen and amide begins to compete successfully with the reduction of the aromatic.

Table I

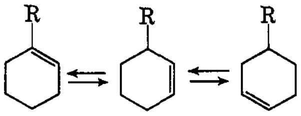
Reduction of Alkyl Benzenes in Methyl-, Ethyl-, and *n*-Propylamine at −7°

Aromatic compound	—Product composition (% 1-olefin)[a,b]— MeNH$_2$	EtNH$_2$	*n*-PrNH$_2$
Toluene	59[c,d]	61 (13)	75 (14)
Isopropylbenzene	47	58 (3)	73 (35)
t-Butylbenzene	42	56 (1)	77 (35)

[a] The values listed are the percentage of the 1-olefin relative to the total olefinic content. The difference between the value given and 100% represents the percentage distribution of the 3- and 4-olefins except in those cases where aromatic was recovered. [b] The values in parentheses represent the amount of aromatic recovered. [c] The values in this table represent an average value of two trials. None of the olefin percentages differed by more than 2% in these trials. [d] All analyses in this table were by v.p.c. Either a Perkin-Elmer Model 154C equipped with a 12-ft. column packed with β,β'-oxydipropionitrile on C-22 firebrick or an Aerograph A-110-C equipped with a 14-ft. column was used.

In many cases, ethylamine becomes the solvent of choice where great selectivity is desired.

It is unlikely that the increase in 1-olefin observed when the solvent is varied from methyl- to *n*-propylamine (Table I) can be attributed to varying base strengths of the solvent, since the latter is almost identical in the case of these three amines. On the other hand, the steric bulk of the three amines is definitely increasing as the alkyl substituent is varied from methyl to *n*-propyl. This may be an important factor in determining product ratios, since these amines are functioning as the protonating agent for the anion intermediates. It seemed possible that, as the reaction became slower owing to employment of a bulky solvent like *n*-propylamine, more time would be provided for the establishment of an equilibrium between the monoolefinic products.[4] If this equilibrium were slow in establishment, it seemed reasonable that a bulky pro-



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[1] (a) This is paper VIII in a series entitled "Reduction of Organic Compounds by Lithium in Low Molecular Weight Amines"; (b) R. A. Benkeser, M. L. Burrous, J. J. Hazdra, and E. M. Kaiser, *J. Org. Chem.*, **28**, 1094 (1963).

[2] R. A. Benkeser, R. K. Agnihotri, and M. L. Burrous, *Tetrahedron Letters*, **16**, 1 (1960).

[3] R. A. Benkeser, R. E. Robinson, D. M. Sauve, and O. H. Thomas, *J. Am. Chem. Soc.*, **77**, 3230 (1954).

[4] A. P. Krapcho and A. A. Bothner-By [*ibid.*, **81**, 3658 (1959)] have shown that the rate of reduction of benzene by lithium in ammonia and alcohol is roughly twenty-seven times as fast when ethanol rather than *t*-butyl alcohol is employed.

TABLE II

REDUCTIONS OF AROMATIC COMPOUNDS TO MONOOLEFINS IN MIXED AMINE SOLVENTS

	Aromatic	Amine solvents (ml.)	1-Alkylcyclohexenes,[a,b] %	3- + 4-alkylcyclohexenes, %
(1)	Toluene	$MeNH_2$ (100) Me_2NH (100)	69 (60)	30[c] (40)
(2)	Toluene	$MeNH_2$ (100) Me_2NH (400)	76 (60)	24 (40)
(3)	Cumene	$MeNH_2$ (45) *n*-$PrNH_2$ (300)	56 (46)	44 (54)
(4)	Cumene	$MeNH_2$ (100) *i*-$PrNH_2$ (100)	65 (46)	19[c] (54)
(5)	Cumene	$MeNH_2$ (50) Morpholine (150)	88 (46)	12 (54)
(6)	Cumene	$H_2N(CH_2)_2NH_2$ (75) Morpholine (100)	87 (76)	12[c] (19[c])
(7)	Cumene	$MeNH_2$ (50) Me_3N (200)	48 (46)	51 (54)
(8)	Cumene	$MeNH_2$ (75) Et_2O (75)	50 (46)	50 (54)
(9)	Cumene	$MeNH_2$ (75) *t*-Octylamine (75)	53 (46)	45[c] (54)
(10)	Cumene	$EtNH_2$ (150) Me_2NH (160)	85 (73)	15 (27)
(11)	Cumene	$EtNH_2$ (200) Me_3N (100)	68 (73)	32 (27)
(12)	*t*-Butylbenzene	$EtNH_2$ (200) Me_2NH (220)	80 (70)	13[d] (30)
(13)	*t*-Butylbenzene	$H_2N(CH_2)_2NH_2$ (100) Morpholine (200)	86 (70)	14 (22)[c]
(14)	Biphenyl	$MeNH_2$ (75) Morpholine (150)	92 (49)	8 (36)[c]
(15)	Naphthalene	$EtNH_2$ (250) Me_2NH (250)	80[h]	20[i]
(16)	β-Phenylethanol	$EtNH_2$ (150) Morpholine (150)	88 (83)[f]	12 (9)[c,g]
(17)	Acetophenone	$MeNH_2$ (200)	70[e]	
(18)	Acetophenone	$H_2N(CH_2)_2NH_2$ (200)	34[e]	
(19)	Acetophenone	$H_3N(CH_2)_2NH_2$ (100) Morpholine (200)	55[e]	

[a] The values in parentheses are the isomer distributions observed when only the pure primary amines were used as solvent. [b] The percentages given represent the isomer distributions obtained. [c] Saturated compound made up the remainder of the product. [d] The remainder of the product recovered was aromatic. [e] Reduction in methylamine was carried out by using 6 equiv. of lithium; 4 equiv. of lithium was used in ethylenediamine and ethylenediamine–morpholine. Reduction carried out in 67 ml. of methylamine and 134 ml. of morpholine with 6 equiv. of lithium resulted in a 90% yield of product. The product referred to in each of these entries is methyl-1-cyclohexenylcarbinol. [f] The product referred to is β-(1-cyclohexenyl)ethanol. [g] The products referred to here are the β-(3- and 4-cyclohexenyl)-ethanols. [h] The product here was $\Delta^{9,10}$-octalin. [i] This product was $\Delta^{1,9}$-octalin.

tonating agent might provide more time for the anion intermediates to rearrange to the most thermodynamic form in which the alkyl group is situated on the double bond.

In order to test this hypothesis, the reductions were attempted in mixtures of primary and secondary amines (see Table II). It was indeed found that the addition of secondary amines like dimethylamine and morpholine to the primary amine solvents usually had a profound effect in increasing the percentage of 1-olefin formed.[5] Certain primary amines like isopropylamine and *t*-octylamine seemed to have some effect also, but tertiary amines (*e.g.*, trimethylamine) and diethyl ether seemed to have have little influence. This discovery has extreme significance in the utilization of the lithium–amine reducing agent as a tool in organic syntheses. As will be noted in Table II the employment of secondary amine diluents permits one to carry out reductions with the lithium–amine reagent in a much more selective fashion. Thus the yield of 1-isopropylcyclohexene was practically doubled when the reduction was carried out in a 3:1 (v./v.) morpholine–methylamine system (entry 5, Table II). The same was true of 1-cyclohexylcyclohexene from the reduction of biphenyl (entry 14, Table II). Likewise the yield of $\Delta^{9,10}$-octalin from the reduction of naphthalene was increased from 52 to 80% by the addition of dimethylamine. The other product (20%) in this reduction was $\Delta^{1,9}$-octalin.

In a few cases the addition of a secondary amine had only a negligible effect on the isomer ratio of the products. In the reduction of β-phenylethanol in ethylamine, the addition of morpholine increased the proportion of β-(1-cyclohexenyl)ethanol from 83 to 88%. On the other hand, when the same reduction was carried out in pure methylamine only 70% of β-(1-cyclohexenyl)ethanol was obtained. This points again to the greater selectivity which is usually achieved in ethylamine compared to methylamine. In almost every case studied thus far, the addition of secondary amines had a salutary effect in increasing the proportion of 1-olefin. An additional advantage to the mixed amine systems is that the volatility of the solvent system is diminished making for greater ease of handling.

It is particularly interesting that at least a small amount of the primary amines like methyl- or ethylamine or ethylenediamine is needed for the reduction to proceed at any appreciable rate. This is vividly illustrated in Table III which lists the isomer distributions

TABLE III

REDUCTION OF CUMENE IN VARIOUS DILUTIONS OF METHYLAMINE–DIMETHYLAMINE

Solvent composition (volume % dimethylamine in methylamine)	1-Isopropylcyclohexene,[a] %	3- + 4-Isopropylcyclohexene,[a] %
33[b]	55	45
50[c]	68	32
80[d]	77	23
93[e]	82	18
96[f]	Dihydro products + cumene	
100[g]	No reduction	

[a] These percentages represent the olefin distribution in the product. [b] Cumene (0.1 mole) and 0.44 g.-atom of lithium used in 100 ml. of Me_2NH and 200 ml. of $MeNH_2$. [c] Cumene (0.1 mole) and 0.44 g.-atom of lithium used in 200 ml. of Me_2NH and 200 ml. of $MeNH_2$. [d] Cumene (0.1 mole) and 0.44 g.-atom of lithium used in 800 ml. of Me_2NH and 200 ml. of $MeNH_2$. [e] Cumene (0.05 mole) and 0.2 g.-atom of lithium used in 350 ml. of Me_2NH and 25 ml. of $MeNH_2$. [f] Cumene (0.1 mole) and 0.4 g.-atom of lithium used in 160 ml. of Me_2NH and 8 ml. of $MeNH_2$. [g] Cumene (0.05 mole) and 0.22 g.-atom of lithium used in 150 ml. of Me_2NH.

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(5) We wish to emphasize that, while we were led to try the secondary amine diluents as a result of considerations regarding steric hindrance to protonation, their success does *not necessarily* prove the validity of this hypothesis. It is entirely possible that the secondary amines exert their influence by an entirely different mechanism. Indeed, there are certain difficulties associated with the concept of steric hindrance to protonation by the secondary amines of which we are well aware. In this paper we are simply reporting the reasoning process which prompted us to try diluting the primary amine solvents with other additives.

obtained in the reduction of cumene as the volume per cent of methylamine–dimethylamine was systematically varied. Two things are apparent from the data. First, the percentage of 1-olefin increases as the quantity of dimethylamine increases, and secondly the limit is reached at about 93% dimethylamine. In pure dimethylamine, very little reduction occurs. Similarly, reduction in pure isopropylamine and pure morpholine was found to proceed very slowly or not at all. At least small amounts of the low molecular weight aliphatic amines seem essential in these reductions to solubilize some of the lithium metal. The lithium appears to be quite insoluble in secondary and branched chain amines.

In order to ascertain whether the addition of secondary amines was permitting equilibration of the isomeric olefins as depicted in eq. 2, the equilibrium distribution of the methylcyclohexenes and *t*-butylcyclohexenes was determined. This was accomplished by equilibrating pure 1-methyl- and 4-methylcyclohexene as well as pure 1-*t*-butyl- and 4-*t*-butylcyclohexene and mixtures of varying composition. The results are listed in Table IV. The most favorable conditions for equilibration was found to be refluxing the olefins in glacial acetic acid containing catalytic quantities of *p*-toluenesulfonic acid. An average value taken from Table IV would be 91–94% 1-methylcyclohexene at equilibrium and 76–79% 1-*t*-butylcyclohexene. As might have been predicted, the results indicate that a methyl group imparts greater thermodynamic stability to 1-methylcyclohexene than does a *t*-butyl group in the same relative position.

Table IV

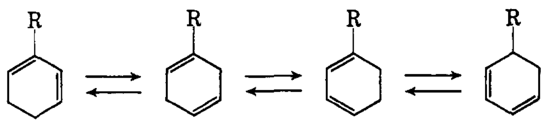
Equilibration of Methyl- and *t*-Butylcyclohexenes

Original composition, %	Reflux time, hr.	Final composition, %
1-Methylcyclohexene, 100	96	1-Methylcyclohexene,[a] 91
1-Methylcyclohexene, 100	113	1-Methylcyclohexene, 94
4-Methylcyclohexene, 100	122	1-Methylcyclohexene, 77
1-Methylcyclohexene, 70 4-Methylcyclohexene, 30	96	1-Methylcyclohexene, 84
1-Methylcyclohexene, 88 4-Methylcyclohexene, 12	163	1-Methylcyclohexene, 93
t-Butylcyclohexene, 100	184	1-*t*-Butylcyclohexene, 76 3-*t*-Butylcyclohexene, 14 4-*t*-Butylcyclohexene, 10
4-*t*-Butylcyclohexene, 100	238	1-*t*-Butylcyclohexene, 67 3-*t*-Butylcyclohexene, 17 4-*t*-Butylcyclohexene, 16
1-*t*-Butylcyclohexene, 75 3-*t*-Butylcyclohexene, 18 4-*t*-Butylcyclohexene, 7	167	1-*t*-Butylcyclohexene, 79 3-*t*-Butylcyclohexene, 13 4-*t*-Butylcyclohexene, 8
1-*t*-Butylcyclohexene, 39 3-*t*-Butylcyclohexene, 36 4-*t*-Butylcyclohexene, 18 *t*-Butylcyclohexane, 7	24	1-*t*-Butylcyclohexene, 72 3-*t*-Butylcyclohexene, 13 4-*t*-Butylcyclohexene, 6 *t*-Butylcyclohexane, 9

[a] This value shows the percentage of 1-olefin relative to total olefin. On prolonged refluxing small amounts of aromatic and unknown were observed.

It will be noted from Table II (entry 13), that an ethylenediamine–morpholine solvent mixture results in an 86% distribution of 1-*t*-butylcyclohexene. This value lies above the equilibrium value obtained for this isomer as listed in Table IV, and would thus cast serious doubt upon the importance of eq. 2 under actual reduction conditions.

To test further the possibility that equilibration of the type shown in eq. 2 was occurring during the reductions, an attempt was made to isomerize 4-methylcyclohexene (an isomer we have shown to be thermodynamically unstable relative to 1-methylcyclohexene) in the presence of lithium methylamide in methylamine. After 6 hr., which might be considered an average time for lithium–amine reduction, little or no isomerization had occurred. Hence, it is our current belief that the monoolefins produced in the lithium–amine reductions are formed under essentially *nonisomerizing conditions*.[6] The isomer distribution of monoolefins must thus be predetermined by the nature and concentrations of the precursors, which, upon reduction, produce the monoolefins. These precursors are very likely cyclohexadienes, that are in a rapid and mobile equilibrium.



Future papers in this series will take up the nature and importance of these cyclohexadienes in determining the final olefin composition.

Experimental

General Procedure for the Reduction of Aromatic Compounds in Mixed Amine Solvents.—Five equivalents of lithium were added to a solution of the aromatic compound in the mixed amine solvent. After the metal had disappeared, the amines were evaporated. Water and ether were added, and the ethereal extracts were dried and distilled. When the primary amine solvent boiled above room temperature (*e.g.*, ethylenediamine), water and ether were added immediately after the metal disappeared with no attempt being made to remove the solvents. The ethereal layer was then neutralized with dilute hydrochloric acid before drying and distilling. The results of all of the reductions run in mixed amine solvents are listed in Table II. The following procedure for the reduction of biphenyl can be taken as typical of this method.

Reduction of Biphenyl in Methylamine–Morpholine.—In a 500-ml. flask was placed 15.4 g. (0.1 mole) of biphenyl in a solvent consisting of 75 ml. of methylamine and 150 ml. of morpholine. A total of 7.7 g. (1.1 g.-atoms) of lithium was added to this solution and was entirely consumed after stirring at room temperature for 12 hr. After the methylamine was evaporated, water was added slowly to the cooled flask. The ethereal extracts were neutralized with dilute hydrochloric acid. Distillation of the ethereal extracts gave 7.9 g. of liquid (48%) along with a small amount of unreduced biphenyl. See Table II for analysis of the distillate.

Analyses of Olefin Mixtures.—All olefin mixtures encountered were analyzed by vapor phase chromatography. Retention times were compared with those of authentic samples prepared by unequivocal methods described below.

Since considerable efforts were expended to obtain pure, authentic samples for comparison, the boiling points and refractive indices of these olefins have been included in Table V, along with the literature values when these were available.

Preparation of Authentic Monoolefins.—All 1-alkylcyclohexenes were prepared by the dehydration of the alkylcyclohexanol with iodine as described by Mosher.[7] The alcohols were prepared by treating cyclohexanone with the appropriate Grignard reagent. Table V lists the physical properties of these alkenes.

The 3-alkyl cyclohexenes were all prepared by a method described by Biggerstaff, *et al.*[8] Table V lists the physical constants of these alkenes.

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[6] It is likely, however, that some isomerization can and does occur when these reductions are carried out in ethylenediamine at elevated temperatures [L. Reggel, S. Friedman, and I. Wender, *J. Org. Chem.*, **23**, 1136 (1958)].

[7] W. A. Mosher, *J. Am. Chem. Soc.*, **62**, 552 (1940).

[8] W. R. Biggerstaff, *et al.*, *J. Org. Chem.*, **19**, 934 (1954).

TABLE V

PHYSICAL CONSTANTS OF PURE SAMPLES OF ALKYL CYCLOHEXENES

Compound	B.p., °C.	$n^{20}{}_D$
1-Methylcyclohexene[b]	108 [109][a]	1.4500 [1.4497][a]
3-Methylcyclohexene[c]	102 [104]	1.4439 [1.4445]
4-Methylcyclohexene[d]	102 [102–103]	1.4419 [1.4418]
1-Ethylcyclohexene[e]	134–136 [134–136]	1.4570 [1.4576]
3-Ethylcyclohexene[f]	132–133 [133]	1.4510 [1.451]
4-Ethylcyclohexene[g]	132 [133]	1.4491 [1.449]
1-Isopropylcyclohexene[h]	155 [155–157]	1.4576 [1.4594]
3-Isopropylcyclohexene[i]	152 [150]	1.4552 [1.4542]
4-Isopropylcyclohexene[j]	155 [150–152]	1.4543 [1.4560]
1-*t*-Butylcyclohexene[g]	170 [173]	1.4623 [1.4638]
3-*t*-Butylcyclohexene[k]	170 [66 (23 mm.)]	1.4595 [1.4593]
4-*t*-Butylcyclohexene[l]	172 [172]	1.4589 [1.4587]
1-Cyclohexylcyclohexene[m]	112 (16 mm.) [88 (4 mm.)]	1.4945 [1.4916]
3-Cyclohexylcyclohexene[n]	109 (13 mm.)	1.4941
4-Cyclohexylcyclohexene[o]	233 [236]	1.4922

[a] The value in brackets represents the literature values. [b] K. Auwers and P. Ellinger, *Ann.*, **387**, 200 (1912). [c] G. Egloff, "Physical Constants of Hydrocarbons," Vol. II, Reinhold Publishing Corp., New York, N. Y., 1940, p. 327. [d] R. T. Arnold, G. G. Smith, and R. M. Dodson, *J. Org. Chem.*, **15**, 1256 (1950). [e] O. Wallach, *et al.*, *Ann.*, **360**, 48 (1908). [f] S. W. Ferris, "Handbook of Hydrocarbons," Academic Press, Inc., New York, N. Y., 1955, p. 33. [g] See footnote *f*, p. 50. [h] See footnote *f*, p. 42. [i] A. Berlande, *Bull. soc. chim. France*, **9**, 644 (1942). [j] H. Pines, R. C. Olberg, and V. N. Ipatieff, *J. Am. Chem. Soc.*, **74**, 4872 (1952). [k] W. R. Biggerstaff, A. P. Menditto, and I. Yokoyama, *J. Org. Chem.*, **19**, 934 (1954). [l] See footnote *c*, p. 343. [m] F. K. Signaigo and P. L. Cramer, *J. Am. Chem. Soc.*, **55**, 3326 (1933). [n] *Anal.* Calcd. for $C_{12}H_{20}$: C, 87.8; H, 12.2. Found: C, 87.53; H, 12.42. [o] W. Schrauth and K. Gorig, *Ber.*, **56**, 1900 (1923).

The 4-alkylcyclohexenes were prepared by the sequence: 4-alkyl phenol → 4-alkyl cyclohexanol → 4-alkyl cyclohexyl acetate → 4-alkyl cyclohexene. The final pyrolysis step was patterned after that described by Bailey.[9] Table V lists the physical constants of these alkenes.

Equilibration of Methyl- and *t*-Butylcyclohexenes (Table IV).—The following isomerizing conditions were studied.

A. **Alumina at 350°.**—Passing an olefinic mixture over an alumina column at 350° caused considerable aromatization. When the temperature was lowered to 220°, little change in composition occurred on several consecutive passes through the column.

B. ***p*-Toluenesulfonic Acid.**—This catalyst proved more efficient and effective than alumina. The olefin was refluxed under nitrogen in acetic acid with a trace of *p*-toluenesulfonic acid. Periodically, about 2 ml. of material was withdrawn, neutralized with excess 10% sodium hydroxide solution, and taken up in 2 ml of ether. The organic layer was analyzed on a Fisher–Gulf partitioner equipped with a 12-ft. β,β′-oxdipropionitrile on C-22 firebrick column operated at 75–85° and at 20 p.s.i.

As noted in Table IV, the amount of 1-methylcyclohexene present in an equilibrium mixture of the methylcyclohexenes was 91–93%. An equilibrium mixture of the *t*-butylcyclohexenes contained 76–79% of the 1-olefin.

In one of the isomerization trials a material balance was calculated. When starting with 15.9 g. of a mixture containing 39% 1-*t*-butylcyclohexene, 11.0 g. of material containing 74% 1-*t*-butylcyclohexene was recovered. Thus the actual amount of 1-olefin increased from 6.2 g. to 8.05 g.

General Directions for the Reductions of Alkylbenzenes in Primary Amines at −7° (Table I).—In each instance lithium wire was added to a solution of alkylbenzene in the amine. The reaction flask was immersed in a cooling bath held at −5 to −9° in the case of ethyl- and *n*-propylamine. Stirring was continued until the lithium had been consumed. With methyl- and ethylamine as solvents, the amine was evaporated before hydrolysis. With *n*-propylamine, water was added directly to the reduction mixture when the metal was completely consumed. At no time during the reductions in *n*-propylamine did the solvent become blue throughout. A blue color was discerned intermittently around the pieces of reacting lithium. The results of these reductions are listed in Table I.

Attempted Isomerization of 4-Methylcyclohexene by Lithium Methylamide.—Lithium methylamide was generated by the reduction of 7.8 g. (0.1 mole) of benzene with 2.8 g. (0.4 g.-atom) of lithium in 200 ml. of methylamine. After all the lithium was gone, 9.6 g. of a mixture of 97% 4-methylcyclohexene and 3% 1-methylcyclohexene was added. After the mixture was stirred for 6 hr., the amine was evaporated. After work-up, an analysis showed 95% 4-methylcyclohexene and 5% 1-methylcyclohexene.

Acknowledgment.—The authors are grateful to the National Institutes of Health and the National Science Foundation for fellowship aid which made this work possible.

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(9) W. J. Bailey and C. King, *J. Org. Chem.*, **21**, 858 (1956).

Stereochemistry of the Deamination of Aziridines[1a,b]

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The reaction of stereoisomers of 2,3-dimethylaziridine with nitrosating agents such as 3-nitro-N-nitrosocarbazole, nitrosyl chloride, and methyl nitrite results in the formation of nitrous oxide and 2-butene with greater than 99% stereoselective deamination. At temperatures below −20°, a yellow intermediate was isolated that exhibited infrared, ultraviolet, and n.m.r. spectra characteristic of an N-nitrosoaziridine. The *trans*-dimethyl intermediate decomposed in a first-order rate with a half-life of 11 min. in methanol at −15°, and it formed nitrous oxide and *trans*-2-butene. The yellow product could be isolated as an oil and purified by low temperature chromatography on Florisil. Certain other nitrosoaziridines, including *cis*-dimethyl, methyl, ethyl, and tetramethyl, were less stable, but nitrosoaziridine itself was more stable. The deamination of aziridines with nitrosyl chloride also led to the formation of aziridine hydrochlorides that were stable at −78°. Although the salts tended to polymerize at higher temperatures, they could be converted to stable derivatives by exchanging anions with silver 2,4,6-trinitrobenzenesulfonate.

Preliminary to a study of the cleavage of nitrogen–carbon single bonds and the synthesis of various β-substituted amines, we have investigated the possibility that N-nitroso derivatives of selected aziridines might be sufficiently stable for isolation and study. It had been shown by Bumgardner, McCallum, and Freeman[2] that aziridine was deaminated readily by 3-nitro-N-nitrosocarbazole to yield ethylene and nitrous oxide. They proposed that the mechanism of the reaction involved either formation of the nitrosamine (1) or a

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(1) (a) Supported in part by Cancer Research Funds of the University of California; (b) abstracted in part from the Ph.D. thesis of R. D. Clark, University of California, 1963.

(2) C. L. Bumgardner, K. S. McCallum, and J. P. Freeman, *J. Am. Chem. Soc.*, **83**, 4417 (1961).