The Structure–Reactivity Relationship of Olefin Reductions with Lithium in Ethylamine. A Comparison of the Ethylamine and Ammonia Systems

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The structure–reactivity relationship for olefins undergoing reduction in the lithium–ethylamine and lithium–ammonia–alcohol media has been determined by the competition procedure. The lithium–ethylamine system shows a selectivity for terminal olefins (a competing isomerization may occur which can be prevented by the addition of an alcohol as the proton source) while the lithium–ammonia–alcohol medium reduces only terminal double bonds. These results and the reactivity sequence found for nonterminal olefins are discussed in terms of the nature of the solvated electrons in the media and the relative stability of the anion-radicals formed from various olefins. Increasing the number of alkyl substituents on the double bond results in a progressive decrease in reduction rate in the lithium–ethylamine system. The reduction sequence found in the cyclic series (norbornene $\gg C_5 > C_7 > C_8 > C_6$) is attributed mainly to ground state strain in the molecules in most of the cases (with the exception of cyclooctene).

Introduction

Liquid ammonia and the lower primary aliphatic amines are of interest because of their ability to dissolve the alkali and the alkaline earth metals.[1] The use of solutions of metal in ammonia for effecting the chemical reduction of organic compounds has attracted considerable attention from both the synthetic and the mechanistic points of view.[2]

The research of Birch and his collaborators[3] has shown that the combination of sodium metal in liquid ammonia with an added alcohol is a synthetic procedure of great utility. The reduction of aromatic ring systems under these conditions leads mainly to the corresponding dihydro system which undergoes no further reduction. This procedure has been modified by Wilds[4] by utilizing lithium instead of sodium and by adding the alcohol last. A kinetic study of the metal–ammonia–alcohol reductions of benzene and substituted benzenes has led to the proposal of a probable mechanism of reduction for these systems in this media.[2,5]

The lithium–aliphatic amine system is also a very useful reduction medium. It has been shown that acetylenic and olefinic bonds are reduced by the lithium–ethylamine combination.[6] When a monosubstituted aromatic compound is reduced with the lithium–amine combination, the products isolated are dependent on the amount of lithium metal utilized. With 4 equivalents of metal, the aromatic is reduced to a mixture of the various isomeric olefins with the isomer distribution dependent on the nature of the group. Excess metal converts the isomeric olefin mixture into the completely saturated cyclohexane system with the 1-alkyl substituted olefin reducing the most slowly.[7] Recently, the lithium–amine–alcohol combination has been reported by Benkeser[8] to yield dihydro compounds from aromatic systems in yields quite comparable to those of the normal Birch procedure.

Owing to the paucity of data on the quantitative nature of the reduction procedure utilizing lithium in ethylamine, a program has been under way for some time to assess the factors controlling the reduction of simple olefinic linkages in this reduction medium.

The lithium–ammonia–alcohol system is included in this study to compare the two media.

Procedure

Because of the low solubility of lithium in ethylamine (initial deep blue color obscures undissolved metal) no attempt was made to measure the absolute kinetics of reduction of various substrates. However, the utilization of competition experiments to determine relative reactivities seemed to be appropriate for a study in this system. Thus, if a mixture of two olefins is reduced in the lithium–ethylamine system, and if it is supposed that the same rate law operates in each case, then the laws governing the reduction of the two olefins may be written

$$-\mathrm{d}(\text{olefin}_1)/\mathrm{d}t = k_1(\text{olefin}_1)(M) \qquad (1)$$

$$-\mathrm{d}(\text{olefin}_2)/\mathrm{d}t = k_2(\text{olefin}_2)(M) \qquad (2)$$

Since the olefins are present in the same reaction mixture, the concentration of metal (M, dissolved or undissolved) and the amount of ethylamine to which they are exposed at any time is the same for both, and division of eq. 1 by eq. 2 yields 3

$$\mathrm{d}(\text{olefin}_1)/\mathrm{d}(\text{olefin}_2) = k_1(\text{olefin}_1)/k_2(\text{olefin}_2) \qquad (3)$$

from which, by integration, is obtained 4

$$\frac{k_1}{k_2} = \frac{\log\,(\text{olefin}_1/\text{olefin}_1^0)}{\log\,(\text{olefin}_2/\text{olefin}_2^0)} \qquad (4)$$

where the superscript zero refers to concentrations at some initial time, t_0.[5,9]

Analyses of the reaction products were performed by the vapor phase chromatographic technique. The total areas corresponding to each olefin and its reduction product were calculated from the chromatogram by the procedure of peak-height times the half-width. The percentage of unreduced olefin in each olefin–hydrocarbon pair was then obtained by dividing the area corresponding to the olefin peak by the total area of the olefin and its reduction product. Equation 4 then reduces to 5

$$k_1/k_2 = \log\,(\%\ \text{olefin}_1)/\log\,(\%\ \text{olefin}_2) \qquad (5)$$

The identification of each chromatogram peak was easily performed by a study of the retention times of authentic samples and in most cases the areas were calculated from nonoverlapping peaks. Any impurities in the starting olefins could readily be ascertained by an analysis of the initial olefin.

Because of the nature of the thermal conductivity detector in the chromatogram, the thermal conductivity of each component should be known. In all calculations from the chromatograms, it was assumed that the

(1) See E. C. Evers, J. Chem. Educ., 38, 590 (1961), for a recent summary and pertinent references on the nature of these solutions.

(2) For a thorough coverage see H. Smith, "Organic Reactions in Liquid Ammonia," Vol. 1, Part 2, Interscience Publishers, A Division of John Wiley and Sons, Inc., New York, N. Y., 1963.

(3) See (a) A. J. Birch, Quart. Rev. (London), 4, 69 (1950); (b) A. J. Birch and H. Smith, ibid., 12, 17 (1958).

(4) A. L. Wilds and N. A. Nelson, J. Am. Chem. Soc., 75, 5360 (1953).

(5) (a) A. P. Krapcho and A. A. Bothner-By, ibid., 81, 3658 (1959); (b) ibid., 82, 571 (1961).

(6) R. A. Benkeser, G. Schroll, and D. M. Sauve, ibid., 77, 3378 (1955).

(7) R. A. Benkeser, J. J. Hazdra, R. F. Lambert, and P. W. Ryan, J. Org. Chem., 24, 854 (1959), and previous papers in this series.

(8) R. A. Benkeser, M. L. Burrous, J. J. Hazdra, and E. M. Kaiser, ibid., 28, 1094 (1963).

(9) G. A. Russell, "Competing Reactions," in A. Weissberger, Ed., "Technique of Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., Vol. VIII, Part 1, 1961, p. 344.

TABLE I
RELATIVE RATE CONSTANTS FOR A SERIES OF SUBSTITUTED CYCLIC OLEFINS

Olefin pair	Relative rate
Cyclopentene/1-methylcyclopentene	25.0
1-Methylcyclopentene/1-ethylcyclopentene	1.4
Cyclohexene/1-methylcyclohexene	25.2
1-Methylcyclopentene/1-methylcyclohexene	2.8
(Cyclopentene/1-ethylcyclopentene)	(35)[a]

[a] Calculated from the other rate ratios.

TABLE II
RELATIVE RATE CONSTANTS FOR ACYCLIC OLEFINS RELATIVE TO CYCLOHEXENE

Olefin	Observation or rate ratio
1-Hexene	Very fast[a]
3,3-Dimethyl-1-butene	17.4
2-Methyl-1-pentene	20
cis-4-Methyl-2-pentene	0.9
trans-4-Methyl-2-pentene	0.8
2,3-Dimethyl-2-butene	Very slow[b]

[a] No detectable reduction of cyclohexene when 39% n-hexane is found. In this case 26% of the cis- and trans-2-hexenes were also formed. [b] No detectable reduction of this olefin was found when 14% of the cyclohexene was reduced.

the relative rates were calculated including the isomeric products as part of the unreduced olefin percentage.

The data in Table III are for olefin reductions performed in ethylamine or ammonia (with an alcohol added as a proton source in several cases) to assess the factors affecting the reduction with respect to media and added proton source.

In Table IV are presented the values obtained by the competition procedure for a series of cyclic unsubstituted olefins. Not all of the values tabulated were obtained in a direct competition with cyclohexene as other cross-competition experiments were also performed. The calculated rate ratios obtained in this manner agreed reasonably well with those determined experimentally; e.g., cyclopentene/cyclohexene = 4.4, cyclopentene/cycloheptene = 1.1. From these experimentally determined values one can calculate cycloheptene/cyclohexene = 4.0, while the experimentally determined value is 3.7.

Discussion

From the data obtained in the competition experiments, which are comparative rather than absolute, the total mechanistic reduction route cannot be ascertained. However, it is possible to compare the

TABLE III
OLEFIN REDUCTIONS IN AMMONIA AND ETHYLAMINE AND THE EFFECT OF ADDED ALCOHOL

Olefin or olefin pair	Medium and condition[a]	Result
1-Hexene	Ethylamine	35.0% n-hexane, 20.0% cis- and trans-2-hexene
1-Hexene	Ethylamine/t-butyl alcohol	31.0% n-hexane
1-Hexene	Ammonia/methanol	17.0% n-hexane
Methylenecyclohexane	Ammonia/methanol	80.0% methylcyclohexane
Norbornene	Ammonia/methanol	About 5% norbornane
{ 1-Hexene[b]	Ammonia/methanol	22.0% n-hexane
{ Norbornene		About 2% norbornane
{ Norbornene[c]	Ethylamine	11.9% n-hexane, 33.8% cis–trans-2-hexene
{ 1-Hexene		42.2% norbornane
{ 1-Hexene[d]	Ethylamine	42.6% n-hexane
{ 3,3-Dimethyl-1-butene		11.9% cis- and trans-2-hexene
		13% 3,3-dimethylbutane
{ 1-Hexene[e]	Ammonia/ethanol	49.0% n-hexane
{ 3,3-Dimethyl-1-butene		13% 3,3-dimethylbutane
Cyclopentene[f]	Ethylamine at −30 to −20°	8.0% cyclopentane

[a] See Experimental section for details of reduction. [b] Relative rate = 11. [c] Relative rate = 4. [d] Relative rate = 4. [e] Relative rate = 4.8. [f] Reaction time of 1 hr.

thermal conductivity of each olefin and its corresponding saturated analog were the same. In several cases samples of known molar concentrations were prepared and analyzed. In these cases the calculated values from the chromatogram agreed within a few per cent with the known molar percentages. Thus, the reliability of the data is assured.

Results

Tables I, II, III, and IV list the pertinent rate data calculated from the vapor phase chromatographic analyses. The probable error of each relative rate constant is 10 to 15% because of the inaccuracy of the area calculations. In many cases the calculated relative rate listed is an average of two determinations. The data for each run in terms of the actual vapor phase analysis is listed under the Experimental section.

In Table I are presented the values for a series of cyclic substituted olefins in order to assess the effect of substituents on the reduction rate in the lithium–ethylamine system.

In Table II the study of acyclic olefins in competition with cyclohexene is reported. Because of the competing isomerization which occurred in several of the terminal olefins, in this and the subsequent tables

TABLE IV
RATE CONSTANTS FOR A SERIES OF CYCLIC UNSUBSTITUTED OLEFINS RELATIVE TO CYCLOHEXENE

Cycloalkene[a]	$k/k_{cyclohexene}$
Norbornene	Very fast[b]
Cyclopentene	4.4
Cycloheptene	3.7
cis-Cyclooctene	1.5
(Cyclohexene)	1.0
Cyclopentene[c]	1.0

[a] All performed using ethylamine as the solvent and the proton source except where noted. [b] No detectable reduction of cyclopentene when 40% norbornane is formed. [c] Performed in the presence of t-butyl alcohol.

results in the lithium–ammonia–alcohol and the lithium–ethylamine systems (with and without added alcohol) in terms of reduction ability with respect to olefin structure. This permits one to assess the possible factors controlling reduction in these systems and to point out any mechanistic similarities.

Several factors which are undoubtedly of considerable importance in the over-all reduction mechanism of olefins are: (1) the ease of formation of the anion-radical arising by monoelectron addition to the double

bond (steric and inductive effects), (2) the stabilization of the anion-radical by solvation forces, and (3) the nature of the proton addition step.[2,3,5] The relative importance of each of these factors is quite difficult to assess as they are somewhat interrelated.

The effect of an alkyl substituent on the reduction rate can be seen by inspecting the data presented in Table I. The effect of the methyl group on lowering the reduction rates of the cyclopentene and the cyclohexene systems is about the same and the substitution of an ethyl group for the methyl group exerts very little effect on the reduction rate. This alkyl group effect has previously been reported by Benkeser.[7]

The more striking effect of the substituent can be seen from the data in Table II. The competition of cyclohexene with 2,3-dimethyl-2-butene shows that the tetrasubstituted double bond is reduced exceedingly slowly. The competition of acyclic olefins such as *cis*- and *trans*-4-methyl-2-pentene with cyclohexene illustrates that the acyclic disubstituted double bond reduces at about the same rate as the cyclic double bond in cyclohexene.

From the data for 1-hexene *vs.* cyclohexene it can be seen that the lithium–ethylamine medium is highly selective in its reducing ability. Although competing isomerization to the *cis*- and *trans*-2-hexenes occurs in this case, no reduction of the cyclohexene could be detected. The greater ease of various substituted terminal olefins to reduction is also illustrated by the competition experiments of 3,3-dimethyl-1-butene and 2-methyl-1-pentene with cyclohexene. Both of these olefins are reduced much more rapidly than the cyclohexene, although competing isomerization is again found in the 2-methyl-1-pentene case. The isomerization occurring in these cases can be completely suppressed by the use of an alcohol as a proton source.[8]

The reduction of terminal olefins has been reported with sodium and methanol in liquid ammonia, but in no cases could a nonterminal olefin be reduced.[10,11] The reduction of 1-hexene in the lithium–ammonia–alcohol medium (stoichiometric amounts of lithium) yielded 17% reduction to *n*-hexane. Several other terminal olefins were effectively reduced to the saturated hydrocarbons and these results are given in Table III. In these reductions no isomeric olefins were detected. A competition of 1-hexene with norbornene in the lithium–ammonia–methanol system showed about 22% reduction of 1-hexene while very little norbornene was reduced (about 2%). This is to be compared with the data for the same olefin pair in the lithium–ethylamine medium listed in Table III in which 42.2% reduction of norbornene resulted while only 11.9% *n*-hexane was produced.

The data presented illustrate that terminal olefins are reduced rapidly by lithium in ethylamine (with competing isomerization, when possible) compared to disubstituted nonterminal olefins, and that the lithium–ammonia–alcohol system shows a marked selectivity for terminal olefins (without any isomerization). The greater ease of reduction of terminal olefins in both media may possibly reflect the greater stability of the anion-radical derived from the terminal olefins (primary carbanion and *sec*- or *t*-radical character) in contrast to the anion-radical formed from internal disubstituted olefins (*sec*-carbanion and *sec*-radical character).[3] Steric hindrance to effective solvation in the anion-radical derived from internal disubstituted olefins might also tend to destabilize this adduct.

The reduction similarity for terminal olefins in the

lithium–ammonia–ethanol and lithium–ethylamine systems can be seen by comparing the relative reactivities of 3,3-dimethyl-1-butene and 1-hexene as shown in Table III. The relative rates of reduction are almost the same in these two media although in ethylamine the isomerization of 1-hexene occurred.

The operation of a similar reduction mechanism in the ammonia and the ethylamine media seems reasonable because of the similarities of the many physical properties of alkali metals in ammonia and the lower primary aliphatic amines.[1,12] In ammonia solutions the solvated electrons are the dominant species suggesting highly solvated "more stable" electrons. In methylamine solutions, the monomer species is the dominant species, suggestive of less highly solvated or "less stable" electrons. Thus, the solvated electrons in the ethylamine might be considered as more "energetic" electrons in comparison with those in the ammonia system which are more effectively solvated.

In the ammonia medium the formation of the lower energy anion-radical from terminal olefins is possible and it undergoes a rapid protonation, but the higher energy anion-radical from disubstituted double bonds is difficult to form (even in the highly strained norbornene only a slight reduction occurs with ammonia and alcohol). The more "energetic" electrons in the ethylamine medium are also able to add to other double bonds of the nonterminal type to lead to higher energy anion-radicals.

The higher boiling point of the ethylamine ($17°$) compared to ammonia ($-33°$) would also seem to be of considerable importance in the reduction since Benkeser[13] has shown that the reduction of di- and tri-substituted double bonds with lithium in ethylamine is suppressed at $-78°$. This may reflect a lowering of rate with temperature or a decreased solubility of the lithium metal with a preponderance of undissolved lithium metal present (a nonreducing species). Cyclopentene was found to undergo a slow reduction at $-20°$ to $-30°$ with lithium in ethylamine although it would be expected to undergo no reduction in the lithium–ammonia–alcohol system at this temperature. Thus the temperature decrease lowers the rate but does not suppress the reduction completely.

From the results presented in Table IV it can be seen that the ring size has a small but significant effect on the ease of reduction of the double bond. The relative order of reduction in this sequence of cycloalkenes is norbornene $>>$ C_5 $>$ C_7 $>$ C_8 $>$ C_6. The rate of reduction of norbornene is very much faster than that of cyclopentene as no detectable reduction of cyclopentene occurred in a competition experiment in which 40% reduction to norbornane occurred.

The effect of angle strain at the double bond can readily be ascertained from the comparison of the relative reactivity of cyclopentene and norbornene.[14] The strain in norbornene has been attributed to angle strain in the molecule and this angle strain is relieved during the reduction process.[15] The strain–energy relationship for the cycloalkanes is C_8 $>$ C_5 $>$ C_7 $>$ C_6.[16] The heat of hydrogenation sequence for these cyclic olefins is C_6 $>$ C_5 $>$ C_7 $>$ C_8.[17] The strain in

(10) H. Greenfield, R. A. Friedel, and M. Orchin, *J. Am. Chem. Soc.*, **76**, 1258 (1954).

(11) T. J. King, *J. Chem. Soc.*, 898 (1951).

(12) M. C. R. Symons, *Quart. Rev.* (London), **13**, 99 (1959).

(13) R. A. Benkeser, G. Schroll, and D. M. Suave, *J. Am. Chem. Soc.*, **77**, 3378 (1955).

(14) See J. G. Traynham, *J. Org. Chem.*, **25**, 833 (1960), for a comparison of norbornene and norbornadiene reductions in the lithium–ethylamine system.

(15) P. von R. Schleyer, *J. Am. Chem. Soc.*, **80**, 1700 (1958).

(16) (a) V. Prelog, *Bull. soc. chim. France*, 1433 (1960); (b) J. Coops, H. van Camp, W. A. Lanbregts, J. Visser, and H. Dekker, *Rec. trav. chim.*, **79**, 1226 (1960).

(17) R. B. Turner and W. R. Meadow, *J. Am. Chem. Soc.*, **79**, 4133 (1957), and references cited therein.

the cycloalkenes has been estimated by Traynham.[18] Using the heat of formation data of Finke[19] for cyclooctane, and the heat of hydrogenation data for cyclooctene,[17] one can estimate the strain energy of cyclooctene. The cycloalkenes in order of decreasing strain are: $C_8 > C_5 > C_7 > C_6$.

Thus it appears in the cyclic series, with cyclooctene excluded, that the reduction sequence observed is most readily interpreted as reflecting the greater strain of the double bonds in norbornene, cyclopentene, and cycloheptene compared to cyclohexene.[20] The primary electronated species, the anion-radical, is more readily formed from the more strained cycloalkene (ground state energy to comparable energy transition states is less in the more highly strained olefins). The case of cyclooctene is of interest in that the strain pattern does not follow.[21] This may reflect some transannular hindrance to effective solvation of the anion-radical formed in this system. Further speculation at this time on this point is unwarranted as experimental work is currently under way to shed light on this point.

In the series of acyclic olefin reductions performed in the ethylamine system (with the exception of 3,3-dimethyl-1-butene), the relative ground state stability reflects the ease of reduction of the double bond. The relative order of reduction is: monosubstituted > disubstituted terminal > disubstituted internal > trisubstituted > tetrasubstituted. This sequence parallels to some extent the decreasing order of the heats of hydrogenation. The hydrogenation order suggests the stabilizing influence of alkyl groups on the double bond.[22]

The isomerization found in several cases of the terminal olefins in the lithium–ethylamine reduction is consistent with the equilibration experiments reported by Schriesheim and the latter results also demonstrate the stabilizing effect of alkyl groups on the double bond.[23] The alkyl substituent effect is consistent with an increasing destabilization effect on the anion-radical with an increasing number of alkyl groups. This may be due to inductive and/or steric effects. The small rate difference found in the reduction of cis- and trans-4-methyl-2-pentene is qualitatively consistent with the relative ground state stability (cis a higher energy form than the trans) as is reflected by the heats of hydrogenation of these olefins.[24]

The importance of the nature of the proton source can be seen from the competition experiment of cyclohexene and cyclopentene in the presence and absence of added t-butyl alcohol. In the latter case the reduction rates are about the same compared to a relative rate of 4.3 in the absence of the added alcohol. These data may reflect the greater ease of protonation of the anion-radical from cyclohexene in comparison to the anion-radical from cyclopentene. The greater ease

of solvation of the cyclopentene anion-radical (more planar and more readily solvated) over the cyclohexene anion-radical (more shielded by the additional methylene group) could account for this greater reactivity and cause the rates of formation of the cycloalkanes to be the same.

Benkeser[8] reports the formation of olefinic products in the reduction of monosubstituted benzenes in the presence of alcohol in the lithium–ethylamine system. These could arise from reduction of the unsubstituted double bond in the initially formed dihydro compound without the postulated isomerization to first the conjugated diene and then rapid reduction of the diene.

The applicability of the results recorded for the specific reduction of various double bonds is of some interest from the synthetic standpoint. Certain selective character is shown for terminal double bonds by the lithium–ammonia–alcohol medium or the lithium–ethylamine–alcohol combination

Experimental

The instrument utilized for the vapor phase chromatographic analyses was the Aerograph A-90-P. The analyses were performed using the columns listed in parentheses after the olefins in each table of experimental data. All the columns were 20 ft. in length with 20% of the substrate on 30/60 mesh firebrick, except for the TCP column which was on 60/80 mesh Chromosorb W and are coded as follows: (U) = UCon polar; (S) = silicone Dow 11; (Ag) = silver nitrate on glycerol; (TCP) = tricresyl phosphate.

Typical Competition Procedure in Ethylamine (Cyclopentene–Cyclohexene).—A 250-ml. two-necked flask fitted with a cold finger type condenser, which had a nitrogen inlet at the top, and a dropping funnel was thoroughly flushed with nitrogen. Ethylamine (30 g.) was added to the flask and a mixture of cyclopentene (3.4 g., 0.05 mole) and cyclohexene (8.1 g., 0.1 mole) was placed in the dropping funnel. Lithium (0.7 g., 0.1 g.-atom) ribbon was added to the ethylamine and ice–water was circulated through the condenser by means of a circulating pump. The mixture was stirred magnetically. The system was kept under the nitrogen atmosphere by means of a mercury trap. A blue coloration developed immediately in the ethylamine and, after

Table V

Olefin pair[a]	Reduction, %	
	Run 1	Run 2
Cyclopentene	45.0[b]	24.5
Cyclohexene (U)	12.8	6.0
Cyclopentene	39.2	24.0
Cycloheptene (U)	37.6	20.0
Cyclopentene	42.0	20.0
Cyclooctene (Ag)	16.0	7.0
Cycloheptene	14.0	37.5
Cyclohexene (U)	4.0	9.0
Cyclopentene	47.2	32.6
1-Methylcyclopentene (U)	2.5	1.5
Cyclohexene	26.0	52.5
1-Methylcyclohexene (S)	1.2	3.0
1-Methylcyclopentene	9.7	14.0
1-Methylcyclohexene (U)	3.2	5.8
1-Methylcyclopentene	20.0	. .
1-Ethylcyclopentene (U)	15.0	. .
Cyclopentene (U)	c	. .
Norbornene (S)	40.0	. .
3,3-Dimethyl-1-butene	51.5	. .
Cyclohexene (S)	4.0	. .
cis-4-Methyl-2-pentene	15.0	. .
Cyclohexene (U)	16.2	. .
trans-4-Methyl-2-pentene	8.5	. .
Cyclohexene (TCP)	10.5	. .
2,3-Dimethyl-2-butene	c	. .
Cyclohexene (U)	14.0	. .

[a] All runs were performed using equimolar amounts of each olefin and usually sufficient lithium to effect 50% reduction, except where noted. In some runs the reaction was analyzed before complete reaction of all the lithium metal. [b] Performed using a 2/1 molar ratio of cyclohexene to cyclopentene. [c] None detected.

(18) J. G. Traynham and M. F. Sehnert, J. Am. Chem. Soc. **78**, 4024 (1956).

(19) H. L. Finke, D. W. Scott, M. E. Gross, J. F. Messerly, and G. Waddington, ibid., **78**, 5469 (1956).

(20) See H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962, p. 191, for a study of selective hydroboration of olefins.

(21) See J. Sicher, in "Progress in Stereochemistry," Vol. 3, ed. by P. B. D. De la Mare and W. Klyne, Butterworth, Inc., Washington, D. C., 1962, p. 237, for other relative rates of additions of substrates to cyclic olefins.

(22) (a) J. Hine, "Physical Organic Chemistry," McGraw–Hill Book Co., Inc., New York, N. Y., 1962, p. 18; (b) C. T. Mortimer, "Reaction Heats and Bond Strength," Pergamon Press, Addison–Wesley Publishing Co., Inc., Reading, Mass., 1962, p. 52.

(23) (a) A. Schriesheim, C. A. Rowe, Jr., and L. Naslund, J. Am. Chem. Soc., **85**, 2111 (1963); (b) A. Schriesheim and C. C. Rowe, Jr., ibid., **84**, 3160 (1962).

(24) R. B. Turner, D. E. Nettleton, and M. Perelman, ibid., **80**, 1430 (1958).

stirring for about 15 min., the olefin mixture was added in one portion. The solution remained blue after the addition of the olefin mixture and the undissolved lithium eventually caked into a silvery ball, from which blue streamers emerged as it was agitated around the flask. After 2 hr. the reaction mixture was poured slowly into ice–water and the resulting top layer was separated. The hydrocarbon layer was washed once with ice–water and dried over potassium carbonate. This sample was used for the vapor phase chromatographic analysis. The following analysis was obtained using a UCon polar column.

Cyclopentene reduction		Cyclohexene reduction	
Cyclopentene	55.0%	Cyclohexene	87.2%
Cyclopentane	45.0%	Cyclohexane	12.8%

Other Pairs of Olefins.—Using the experimental procedure described above, the observations summarized in Table V were made.

Several competitive and individual reduction experiments were performed in ethylamine which yielded isomeric olefinic products along with the expected reduction products. The effect

TABLE VI

Olefin or olefin pair[a]	Reduction, %	Isomer and % isomerization
⌠Norbornene	42.2	
⌡1-Hexene (TCP)	11.9	cis- and trans-2-hexene 33.8
⌠Cyclohexene	None	...
⌡1-Hexene (TCP or U)	39.0	cis- and trans-2-hexene 36.0
1-Hexene (TCP or U)	35.0	cis- and trans-2-hexene 20.0
1-Hexene[b]	31.0	None detected
⌠2-Methyl-1-pentene	36.7	2-Methyl-2-pentene 16.7
⌡Cyclohexene (TCP)	2.4	...
⌠1-Hexene (U)	42.6	cis- and trans-2-hexene 11.9
⌡3,3-Dimethyl-1-butene (S)	13	...
⌠Cyclopentene[c]	6.0	...
⌡Cyclohexene	5.8	...

[a] All runs were performed with ethylamine as the solvent and the proton source, except where noted. Lithium was used to effect about 50% reduction in the competition experiment, and the stoichiometric amount of metal was utilized in the noncompetition runs. [b] The olefin was added with an equimolar amount of t-butyl alcohol. [c] The olefins were added with an equimolar amount of t-butyl alcohol to the lithium in ethylamine.

of adding alcohol to the system was also studied. The experiments were all performed according to the previous typical procedure and the results of these experiments are presented in Table VI.

Typical Reduction Procedure in Liquid Ammonia (1-Hexene Reduction).—In a 500-ml., three-necked flask equipped with an ammonia inlet, a Dry Ice condenser, and a dropping funnel were placed 250 ml. of liquid ammonia, and 1-hexene (15 g., 0.18 mole) was added. To this solution was added a portion of the lithium (2.5 g., 0.36 mole), upon which a blue color immediately developed. A portion of methanol (total added, 23 g., 0.72 mole) was added dropwise until the blue coloration was discharged. This process was repeated until all the lithium and the methanol was added. The ammonia was allowed to evaporate partially and the residual ammonia was decomposed by the addition of ice. The top layer was separated and dried over potassium carbonate; weight 5.7 g. (41%). This was analyzed by vapor phase chromatography. The following analysis was obtained using a tricresyl phosphate column: n-hexane, 17.0%; 1-hexene, 83.0%.

The results of other experiments performed in the ammonia medium are recorded in Table VII. No isomeric products were detected in any of the runs performed in this medium.

TABLE VII

Olefin or olefin pair	Reduction, %
1-Hexene (TCP)	17.0
Methylenecyclohexene[a] (U)	80.0
Norbornene[b] (TCP)	5
⌠1-Hexene[c] (U)	49.0
⌡3,3-Dimethyl-1-butene (S)	13.1
⌠1-Hexene[d]	22.0
⌡Norbornene (TCP)	2

[a] Treated successively with two stoichiometric amounts of lithium followed by ethanol addition after each portion to discharge the color. [b] Following the typical procedure for 1-hexene except that 3 equivalents of metal were utilized with methanol as the proton source. [c] Using equimolar quantities of olefins and lithium and ethanol as the proton source. [d] Equimolar amounts of olefins and lithium utilized, with methanol as the proton source.

The Reaction of Triphenylphosphine Oxide with Alkyllithium and Grignard Reagents[1]

By Dietmar Seyferth,[2a] Dean E. Welch,[2b] and James K. Heeren[2c]

The reaction of RCH₂Li in ether or of RCH₂MgBr in refluxing tetrahydrofuran with triphenylphosphine oxide results in formation of benzene and (C₆H₅)₂P(O)CH(R)M (M = Li and MgBr, respectively). Some characteristic reactions of such diphenylphosphinylalkyl organometallic reagents are described. The mechanism of formation of these reagents from triphenylphosphine oxide is shown to involve a very rapid exchange step, (C₆H₅)₃PO + RCH₂M → (C₆H₅)₂P(O)CH₂R + C₆H₅M, followed by a slower (but still rapid) metalation reaction, (C₆H₅)₂P(O)CH₂R + C₆H₅M → C₆H₆ + (C₆H₅)₂P(O)CH(R)M, when M is lithium. Both exchange and metalation steps are slower when M is MgBr.

Our recent work[3] on the mechanism of the reaction of organolithium reagents with phosphonium salts, in which phosphorus bears a full positive charge, prompted further investigations of the action of organolithium reagents on tertiary phosphine oxides, in which phosphorus bears a partial positive charge. Of particular interest to us were those reactions which conceivably might proceed *via* transient pentasubstituted phosphorus intermediates. We report here

on the reaction of alkyllithium and Grignard reagents with triphenylphosphine oxide (TPPO).

A clue that these particular reactions might be of interest was provided by a synthesis used by Wittig and Rieber[4] for tetraphenylphosphonium iodide

$$(C_6H_5)_3PO + C_6H_5Li \xrightarrow{} \xrightarrow{HX} [(C_6H_5)_4P]X$$
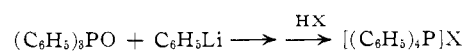
It seemed possible that here a P(V) intermediate, $(C_6H_5)_4PO^- Li^+$, might be involved. In order to obtain further information concerning this reaction, we treated TPPO with alkyllithium reagents.

Addition of 1 molar equivalent of methyllithium to a slurry of TPPO in diethyl ether at room temperature resulted in formation of a reddish brown, homoge-

(1) (a) Presented in part at the Symposium, "Current Trends in Organometallic Chemistry," Cincinnati, Ohio, June 12–15, 1963; (b) preliminary communication: D. Seyferth, D. E. Welch, and J. K. Heeren, *J. Am. Chem. Soc.*, **85**, 642 (1963).

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(3) D. Seyferth, J. K. Heeren, and W. B. Hughes, *J. Am. Chem. Soc.*, **84**, 1764 (1962).

(4) G. Wittig and R. Rieber, *Ann.*, **562**, 187 (1949).