Pyrolysis of the photodimer of VIIIb. The dimer of VIIIb (0.3g.) was heated at 180–185° (metal bath) in a Pyrex test tube for 10 min. The colorless dimer melted with yellow color, and upon cooling the reaction mixture, followed by crystallization, VIIIb was obtained in almost quantitative yield.

GIZA, CAIRO, EGYPT.

[CONTRIBUTION OF THE CENTRAL EXPERIMENT STATION, BUREAU OF MINES, DIVISION OF SOLID FUELS TECHNOLOGY]

Lithium in Ethylenediamine: A New Reducing System for Organic Compounds[1]

LESLIE REGGEL, R. A. FRIEDEL, AND IRVING WENDER

Received January 11, 1957

A new metal-amine reducing system, lithium in ethylenediamine, is described. It reduces aromatic rings to monoölefins and to cycloparaffins; reduces phenols; cleaves ethers; reduces ketones to alcohols; and reduces acetylenes and both terminal and internal olefins to alkanes. It appears to be the most powerful, and perhaps the least selective, of the metal-amine systems.

The present investigation deals with the reduction of organic compounds by the lithium-ethylenediamine system. Most studies with metal-ammonia and metal-amine systems have been carried out using liquid ammonia. Although Kraus[2] predicted in 1953 that methylamine, ethylamine, and ethylenediamine would be valuable solvents for studying the physico-chemical properties of solutions of metals in amines at higher temperatures, ethylenediamine has not hitherto been used in a metal-amine reducing system. The first use of the lower aliphatic amines for metal-amine reductions was recently reported by Benkeser *et al.*,[3] who showed that aromatic rings are reduced to monoölefins by lithium-ethylamine. However, their attempt to replace ethylamine by higher primary amines gave poor yields, perhaps because lithium becomes progressively less soluble in these monofunctional amines as the ratio of nitrogen to carbon decreases. Since ethylenediamine contains one amine group per carbon atom, and since its relatively high boiling point (117°) is a potential advantage, we decided to investigate its use in a metal-amine system. Our results show that the lithium-ethylenediamine system, at 90–100°, is a convenient and effective metal-amine combination for carrying out reductions and cleavage reactions of organic compounds.[4]

EXPERIMENTAL

Materials. Lithium, obtained from the Lithium Corp. of America, was used in the form of one-eighth inch wire.

Anhydrous ethylenediamine (Union Carbide Chemical Co. and Eastman) was purified by heating with sodium for a few days and then distilling; the reaction of sodium with the amine is slow. This once-distilled material was poured directly into the reaction flask without any special precautions to avoid exposure to the atmosphere. (In some experiments, the once-distilled amine was distilled from sodium a second time directly into the dropping funnel on the reaction apparatus; where this material was used, it is referred to as twice-distilled ethylenediamine.)

Diethylenetriamine (Eastman) was purified by distilling it once from a solution of sodium in the amine.

General Procedure. A four-neck flask, or a three-neck flask with a suitable adapter, was fitted with a mercury-sealed double Hershberg stirrer, a thermometer dipping below the surface of the liquid, a spiral reflux condenser with a nitrogen inlet and mercury-sealed outlet, and a straight reflux condenser, 6 to 8 inches long, which was stoppered at the top. (In some experiments, a graduated dropping funnel was so arranged that ethylenediamine could be distilled into the funnel and then added to the flask without exposure to air.) After the apparatus was flushed with nitrogen, the substrate to be reduced and the ethylenediamine were added, the stirrer was started, and the mixture was heated to 90–100°. The lithium was then added in portions through the short reflux condenser; it was added in pieces about 1.5 in. long, about 4 to 8 pieces (0.5–1.0 g.) being added in each portion. The rate of addition of the lithium was controlled by two factors, the hydrogen evolution and the persistence of the dark blue color. Usually the gas evolution was the determining factor, the metal being added during 1.5 to 3 hr., without waiting for discharge of the blue color between portions. The mixture was maintained at 90–100° during addition of the lithium. After all of the metal had been added, the mixture was heated at or just below a gentle reflux for 1 or 2 hr. The mixture was then cooled in ice, and water was added slowly; considerable heat was evolved, and after a little water had been added the mixture usually became almost solid, requiring efficient stirring. After enough water had been added to dissolve most of the solids, the mixture was transferred to a separatory funnel with the aid of water and benzene or ether. The aqueous layer was extracted with the solvent, and the combined organic layers washed with dilute hydrochloric acid, then with saturated sodium chloride solution, dried, and dis-

---

(1) I. Wender and L. Reggel, Abstracts of Papers, 127th Meeting, AMERICAN CHEMICAL SOCIETY, Cincinnati, Ohio, April 1955, page 22N. See also *Chem. Eng. News,* **33**, 1525 (1955).

(2) C. A. Kraus, *J. Chem. Ed.*, **30**, 83 (1953).

(3) R. A. Benkeser, R. E. Robinson, D. M. Sauve, and O. H. Thomas, *J. Am. Chem. Soc.*, **76**, 631 (1954); **77**, 3230 (1955). A preliminary investigation of this topic was mentioned in a paper by R. A. Benkeser, R. E. Robinson, and H. Landesman, *J. Am. Chem. Soc.*, **74**, 5699 (1952).

(4) Recent work in these laboratories has shown that coal, which is difficult to hydrogenate at temperatures below 300°, can be reduced by the lithium-ethylenediamine system.

TABLE I

REDUCTION OF TETRALIN[a]

Experiment	Moles of lithium per mole tetralin	Percent excess lithium[b]	Amine used[c]	Amine, ml.	Yield, percent		
					Octalin	*Trans*-decalin[d]	Tetralin
1	4.4[e]	10	II	150	32.1	—	46.0
2	8.0[e]	100	II	150	68.0	—	31.4
3	4.4	10	II	150	40.0	—	65.2
4	8.0	100	II	375	54.2	32.6	—
5	8.0	100	III	375	96.9	—	—
6	12.2	200	III	375	54.9	34.7	—
7	8.0	100	I	375	57.5	31.9	—
8	8.0[f]	100	I	375	81.8	4.5	—
9	8.0	100	IV[g,h]	375	24.3	—	60.3
10	8.0	100	IV[g,i]	375	27.6	—	56.8
11	8.0[j]	100	I	375	5.7	—	89.4
12	8.0[k]	100	I	375	68.7	18.5	—

[a] In all experiments, 0.20 mole of tetralin was used. Unless otherwise noted, the lithium was added fairly rapidly, during 1 to 2 hr. [b] Percent excess over amount theoretically needed to reduce tetralin to octalin. [c] I, ethylenediamine distilled from sodium and poured into reaction flask; II, ethylenediamine distilled from sodium and then redistilled from sodium directly into apparatus; III, ethylenediamine as received; IV, diethylenetriamine. [d] No *cis*-decalin was formed in any reaction. [e] In these experiments, the tetralin, lithium, and ethylenediamine were mixed and allowed to react. In the other experiments, the lithium was added in portions, as given in the general procedure. [f] Lithium added in small portions during 5 hr.; each portion was allowed to react completely before the next was added. In experiment 7, which is otherwise identical, the lithium was added during 1 hr. [g] Reaction much slower than with ethylenediamine. Solution becomes dark red and then dark brown, but is never blue. [h] Reduction at a temperature of 130–140°. [i] Reduction at a temperature of 155–168°. [j] Sodium, 6–8 mm. shot. The reaction is much slower with sodium than with lithium, and the solution becomes dark brown and quite viscous. [k] In presence of 2.5 moles of ethanol per mole of tetralin.

tilled. (The reaction mixtures from the reductions of phenol and anisole were acidified to prevent any acidic organic materials from being lost in the alkaline aqueous portion.) The products were analyzed by infrared spectroscopy, supplemented in a few cases by ultraviolet or mass spectra.

Convenient quantities were found to be about 375 ml. (5.6 moles) of ethylenediamine,[5] 0.40 mole of a compound containing one double bond, or 0.20 mole of a compound containing two double bonds, and 1.60 moles of lithium, *i.e.*, twice as much lithium as is theoretically needed for the reduction. Since the reaction of lithium with amine to form hydrogen is competitive with the reduction, a better yield from a difficultly reducible compound might be obtained by increasing the amount of lithium still further; in such a case, more amine would probably be needed to prevent the mixture from becoming too viscous.

RESULTS AND DISCUSSION

A study has been made of the reduction of tetralin by lithium in ethylenediamine in an attempt to find the best general conditions for the reaction, and also throw some light on the course of the reaction. The results are shown in Table 1 and the conclusions are summarized below:

1. The extent of reduction increases with an increase in the amount of lithium used. The reaction[6] between a mixture of tetralin, ethylenediamine, and lithium (in 10% excess over the amount theoretically required to reduce tetralin to the octalin stage) gives a 32.1 percent yield of $\Delta^{9,10}$-octalin.[7] Increasing the amount of lithium to 100% excess gives a 68.0 percent yield of octalin.

2. Addition of the lithium in portions increases the amount of reduction, giving both octalin and *trans*-decalin.[8] It seems probable that the increased amount of reduction in the portionwise addition of lithium is due to the metal having a better chance to react with the tetralin, rather than to become lost by reaction with the amine.

---

[5] Because of the corrosive nature and toxicity of ethylenediamine, all operations with it are carried out in a hood. The operator wears rubber gloves, at least up to the point where the ethylenediamine has been diluted with a large quantity of water. Since ethylenediamine will penetrate rubber, the gloves should be rinsed off frequently. These precautions are considered absolutely necessary.

[6] When tetralin and lithium are placed in ethylenediamine and the mixture stirred at room temperature, a very slow evolution of gas takes place at the surface of the lithium. When the mixture is heated to about 85°, however, a violent reaction takes place, with evolution of a considerable amount of hydrogen. It is apparently not possible to prepare a solution of lithium in ethylenediamine, because of the rapid formation of amide.

[7] For simplicity, these samples were analyzed (infrared spectra) as three component mixtures of tetralin, $\Delta^{9,10}$-octalin, and *trans*-decalin. Other octalins were present only in small amounts. We wish to thank Dr. R. A. Benkeser for a copy of the infrared spectrum of pure $\Delta^{9,10}$-octalin.

[8] No *cis*-decalin is found in any of the tetralin reductions. It is known that sodium-ammonia[9] and lithium-ethylamine[10] reduce acetylenes exclusively to *trans*-olefins. Lithium-ethylamine also can reduce tetralin to decalin, although in lower yield than does lithium-ethylenediamine; the configuration of the decalin formed was not reported.[3]

[9] G. W. Watt, *Chem. Revs.*, **46**, 317 (1950).

[10] R. A. Benkeser, G. Schroll, and D. M. Sauve, Abstracts of Papers, 127th meeting, AMERICAN CHEMICAL SOCIETY, Cincinnati, Ohio, April 1955, page 21N; *J. Am. Chem. Soc.*, **77**, 3378 (1955).

3. Addition of lithium at a very slow rate causes a decrease in the yield of reduced material.[11]

4. The yield of reduced material is decreased by the presence of impurities (water and carbonate) in the ethylenediamine. Thus, the use of twice-distilled amine, with complete exclusion of moisture, gives essentially the same results as does the use of once-distilled amine, with some exposure to atmospheric moisture. However, the use of one sample of unpurified amine (as received from the supplier), which may have contained as much as 5% of moisture and carbonate, gave a high yield of octalin, but no decalin. This loss of reductive power is thought to be due to loss of lithium by its reaction with water in the amine. (The use of a very large excess of lithium results in the formation of both octalin and decalin, even with unpurified amine.) Similarly, the presence of added ethanol reduces the proportion of decalin; this is probably caused by the ethanol using up some of the lithium, but having no other effect on the course of the reaction. It is known that in the case of the sodium-liquid ammonia system, addition of a material that can furnish protons, such as water or an alcohol, may materially change the course of the reaction.[9,13] With lithium in ethylenediamine, however, any protons needed for the reduction are probably supplied by the amine, in the absence of any added proton donor; addition of ethanol merely reduces the total amount of reduction by using up some of the lithium.

5. Diethylenetriamine is a poorer reagent for these reductions than is ethylenediamine. Increasing the reaction temperature from 130° to 155° appears to have little effect on the yield obtained with diethylenetriamine.

6. The sodium-ethylenediamine system is a much poorer reagent for reductions than is the lithium-ethylenediamine system. This parallels the findings of Wilds and Nelson,[14] who have shown that lithium in liquid ammonia is a better reducing system than sodium in liquid ammonia; it is also in accord with the work of Benkeser *et al.*,[3] who found that naphthalene gave only polymeric materials when treated with sodium-ethylamine.

Table II reports the reduction of a variety of compounds. It is noteworthy that phenol is reduced to a mixture of cyclohexanone and cyclohexanol.[15]

Anisole reacts vigorously, with gas evolution; the main product is phenol, together with small amounts of Δ^2-cyclohexenone, cyclohexanone, cyclohexanol, cyclohexene, and cyclohexane. The primary reaction is apparently a rapid cleavage of the ether linkage to give methane and phenol; this is followed by a slower reduction of the phenol. Undoubtedly, the phenol would react further if more lithium were used. Similarly, the reaction of lithium and ethylenediamine with di-*n*-hexyl ether gives small amounts of hexanol and hexenes.[17]

Terminal acetylenes and both terminal and internal olefins are reduced to alkanes by lithium and ethylenediamine. In contrast, sodium in liquid ammonia reduces acetylenes to olefins,[9] does not reduce nonconjugated internal olefins at all,[9] and reduces terminal olefins only in the presence of a proton donor.[18] On the basis of the present work, the authors believe that it will be possible to reduce any double or triple carbon to carbon bond with lithium in ethylenediamine. Under conditions where a terminal olefin is not completely reduced, it is largely or entirely isomerized to internal olefins. Subsequent work[19] has shown that this isomerization is catalyzed by the amide $H_2NCH_2CH_2\bar{N}HLi^+$. These reactions, and the corresponding lithium-ethylamine reactions,[10] are the first examples of chemical reduction of a nonconjugated internal olefin.

The other reductions shown in Table II require no comment, except to point out that each is the result of a single experiment.

It seems likely that lithium-ethylamine will prove useful for reduction of aromatic compounds to monoölefins, while lithium-ethylenediamine will be useful for complete saturation of ring systems and for reduction of difficultly reducible materials. Compared to other metal-amine systems, lithium-ethylenediamine appears to be the most powerful and the least selective. However, the high yield of octalin obtained in one experiment (Table 1) does suggest that it may be possible to find conditions under which lithium-ethylenediamine is selective in its action.

The metal-amine reactions with aromatic sys-

---

[11] It has recently been shown[12] that some sodium-ammonia and lithium-ammonia reductions, which fail when the usual procedures are used, can be carried out successfully if the metal is added at a rate rapid enough to cause the separation of a bronze layer.

[12] W. F. Short, unpublished work; W. S. Johnson, B. Bannister, and R. Pappo, *J. Am. Chem. Soc.*, **78**, 6331 (1956). We wish to thank Professor Johnson for sending us a copy of his manuscript in advance of publication.

[13] A. J. Birch, *Quart. Revs.*, **4**, 69 (1950).

[14] A. L. Wilds and N. A. Nelson, *J. Am. Chem. Soc.*, **75**, 5360 (1953).

[15] The present work[1] is thought to be the first report of chemical reduction of a phenol. In subsequent work, Benkeser has found that phenol is reduced by the lithium-ethylamine system.[16]

[16] R. A. Benkeser, C. Arnold, R. F. Lambert, and O. H. Thomas, *J. Am. Chem. Soc.*, **77**, 6042 (1955).

[17] The ether cleavage is probably an elimination reaction catalyzed by the base $H_2NCH_2CH_2\bar{N}HLi^+$, which is formed by the reaction of lithium with the amine.

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

[19] L. Reggel, S. Friedman, and I. Wender, Abstracts of Papers, 129th Meeting, AMERICAN CHEMICAL SOCIETY, Dallas, Tex., April 1956, page 10N.

TABLE II

REDUCTION OF VARIOUS COMPOUNDS BY LITHIUM IN ETHYLENEDIAMINE

	Compound, Moles	Li per Mole Compound, Moles	Ethylenediamine, Ml.	Products	Yield Percent	Yield Recovered Starting Material
$\Delta^{9,10}$-Octalin[a]	0.20	4.0	375	*trans*-Decalin[b]	36.9	55.4
Phenanthrene	0.05	14.4[c]	200	Decahydro- and dodecahydrophenanthrenes[d]	*ca.* 90	1.7
Anthracene	0.05	28.0	300	Dodecahydro- and tetradecahydroanthracenes[e]	*ca.* 95	—
Benzene	0.30	4.8	375	Cyclohexene	51.0	21.6
				Cyclohexane	1.4	
Benzyl alcohol	0.20	16.0	400	Hexahydrobenzyl alcohol	38.5	—
Phenol	0.30	14.0	400	Cyclohexanone	50.0	21.3
				Cyclohexanol	5.5	
				Cyclohexane	Absent	
Anisole	0.40	4.4	375	Phenol	53.9	0.2
				Δ^2-Cyclohexenone	6.5	
				Cyclohexanone	1.6	
				Cyclohexanol	1.1	
				Cyclohexene	1.5	
				Cyclohexane	1.6	
Heptanone-3	0.30	4.0	375	Heptanol-3	29.6	15.1
Di-*n*-hexyl ether	0.20	8.0	400	Hexene-2 or -3	0.5	78.8
				Hexanol[f]	8.4	
Heptene-1	0.32	1.0	300	Heptane	41	32
				Heptene-2	13	
Decene-1	0.30	2.4[c]	150	Decane	47.2	Absent
				Decenes with internal double bond	13.8	
Heptene-2	0.40	4.0	375	Heptane	81.8	
				Heptene-1	Absent	
				Heptenes with internal double bond	2.6	
Heptyne-1	0.20	10.0	300	Heptane	50.9	
				Heptenes	Absent	
				Heptyne	Absent	
Octene-1	0.40	3.0[g]	375	Octane	84.8	
				Octenes with internal double bond	3.4	
Octene-1	0.40	3.0[h]	375	Octane	76.5	
				Octenes with internal double bond	12.5	

[a] Obtained by lithium reduction of tetralin and purified by distillation. Analyses (mass and infrared spectra) indicated 2.1 percent *trans*-decalin, 0.8 percent tetralin, and 97.1 percent octalins, primarily the $\Delta^{9,10}$-isomer. [b] No *cis*-decalin was formed. [c] In these experiments, the substrate, lithium, and ethylenediamine were mixed and allowed to react. In the other experiments, the lithium was added in portions, as given in the general procedure. [d] *Anal.* Calcd. for $C_{14}H_{20}$: C, 89.29; H, 10.71. Calcd. for $C_{14}H_{22}$: C, 88.35; H, 11.65. Found: C, 88.29; H, 10.61. [e] *Anal.* Calcd. for $C_{14}H_{22}$: C, 88.35; H, 11.65. Calcd. for $C_{14}H_{24}$: C, 87.42; H, 12.58. Found: C, 87.97; H, 11.87. [f] Isomer not determined. [g] Lithium added during 32 min. [h] Lithium added in small portions, during 5 hr. Each portion was allowed to react completely before the next was added.

tems have usually been regarded as taking place via 1,4-additions;[13] further reaction occurs only after the initial product has rearranged to a conjugated system. The reduction of the last remaining double bond, which can only be a 1,2-addition, either does not take place (metal-ammonia) or is slow (lithium-ethylamine). Reduction of an isolated double bond with lithium and ethylenediamine is a fast reaction. It is possible that 1,2- and 1,4-additions may take place concurrently in the initial stages. Since high yields of alkanes are obtained from straight chain olefins, the relatively low yield in the reduction of octalin may be due to the presence of a steric factor.

Wilds and Nelson[14] have discussed the superiority of lithium in liquid ammonia to sodium in liquid ammonia for the reduction of various compounds. Benkeser *et al.*[3] have pointed out "the potency and uniqueness" of the lithium-ethylamine combination in the reduction of aromatic hydrocarbons. In a similar way, lithium-ethylenediamine is superior to sodium-ethylenediamine.

Acknowledgments. We wish to thank Leonard Shufler and John Queiser for infrared analyses and Raphael Raymond for some of the reduction experiments.

BRUCETON, PA.