

[CONTRIBUTION FROM CENTRAL EXPERIMENT STATION, BUREAU OF MINES, U. S. DEPARTMENT OF THE INTERIOR]

The Lithium-Ethylenediamine System. II. Isomerization of Olefins and Dehydrogenation of Cyclic Dienes^{1,2}

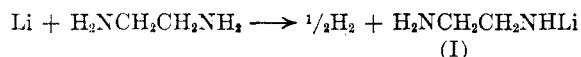
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The solution formed from the reaction of lithium with ethylenediamine, which probably contains $\text{H}_2\text{NCH}_2\text{CH}_2\text{NHLi}$, is capable of rapidly and quantitatively isomerizing a terminal olefin to an internal olefin. A cyclic diene (such as 4-vinylcyclohexene) is converted to the corresponding aromatic hydrocarbon, with evolution of hydrogen gas; this reaction takes place slowly even at room temperature. The corresponding sodium compound, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NHNa}$, isomerizes olefinic double bonds at a very slow rate; however it will rapidly aromatize a cyclic diene in which the double bonds are already conjugated and in the ring.

Recent work has shown² that lithium in ethylenediamine is a powerful reducing system. Many substances, including olefins, phenols, and even coal,³ which are difficult to reduce by chemical means, are hydrogenated by lithium in ethylenediamine. It has also been observed² that incomplete reduction of a terminal olefin by the lithium-ethylenediamine system leads to a mixture of alkane and internal olefin. The present work was therefore initiated to study the isomerization of olefins; it has led to the discovery of an unusual low-temperature, base-catalyzed dehydrogenation reaction.¹

Isomerization of olefins. When metallic lithium is added to ethylenediamine at a temperature of 80–115°, there is a rapid reaction, with evolution of hydrogen.⁴ A dark blue material forms at the surface of the metal; when the solution is stirred, the color quickly spreads throughout the liquid. On continued heating, the blue color gradually fades and disappears, leaving a colorless or pale yellow solution which may contain a small amount of white solid in suspension. It seems reasonable to write:



N-Lithioethylenediamine, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NHLi}$ (I), which is formed in this manner, functions as a catalyst for the isomerization of olefins. When 1-octene is heated with a solution of I in ethylenediamine, the material which is recovered (in 90% yield) consists entirely of internal olefins. Neither

1-octene nor octane can be detected; the absence of octane is evidence that metallic lithium is not present in the medium, since both terminal and internal olefins are readily reduced by lithium in ethylenediamine.^{2,5} In a similar manner, 4-methylcyclohexene is isomerized to 1-methylcyclohexene.

Dehydrogenation of cyclic dienes. In view of these results, it seemed of interest to investigate the isomerization of a cyclic diene, in the thought that hydrogen transfer might lead to a disproportionation.⁶ Accordingly, 4-vinylcyclohexene was added to a solution of *N*-lithioethylenediamine (I). There was a rapid evolution of hydrogen; the product, obtained in 87% yield, consisted entirely of ethylbenzene. This dehydrogenation reaction is apparently general; *d*-limonene (1-methyl-4-isopropenylcyclohexene) and α -phellandrene (2-methyl-5-isopropyl-1,3-cyclohexadiene) both yield *p*-cymene. The dehydrogenation reaction with (I) is essentially quantitative in a few minutes at 100°; at room temperature it is much slower, but dehydrogenation does take place (3.6% yield of *p*-cymene from *d*-limonene after 1.5 hr.⁷

The reaction of sodium with ethylenediamine is much slower than that of lithium. The final solution of *N*-sodioethylenediamine, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NHNa}$ (II) is dark brown and quite viscous. It might be expected that II would have properties similar to those of I. However, there are striking differences. When 1-octene is treated with this solution of II for 6 hr., the yield of internal olefins is 2.2%; under similar conditions, I effects complete isomerization in an hour or less. II will not catalyze the conversion of *d*-limonene (unconjugated double bonds) to *p*-cymene; however, it will de-

(1) Presented before the Division of Organic Chemistry at the 129th Meeting, American Chemical Society, Dallas, Tex., April 1956.

(2) The paper by L. Reggel, R. A. Friedel, and I. Wender, *J. Org. Chem.*, **22**, 891 (1957), is regarded as Part I of this series.

(3) L. Reggel, R. Raymond, S. Friedman, R. A. Friedel, and I. Wender, *Fuel*, **37**, 126 (1958).

(4) It has recently been observed that with some samples of ethylenediamine, the reaction of lithium is very slow at first. Since ethylenediamine is notoriously difficult to purify, the difference in reaction rate may be due to some impurity. Addition of a drop of water did not increase the rate of the slow-reacting material. However, the solutions ultimately obtained seem to have the same properties.

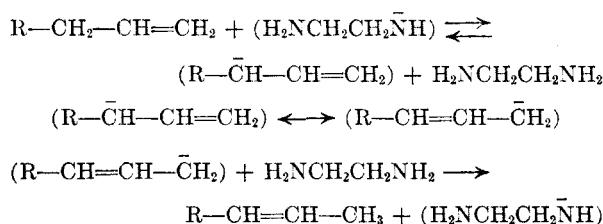
(5) The reaction depends in some manner upon the concentration of I; 1-octene is completely isomerized by a solution which is 1.06 molar in I, but is unchanged by a solution which is 0.33 molar in I.

(6) Compare the conversion of *d*-limonene to a mixture of *p*-cymene and *p*-menthane by palladium and platinum catalysts; Zelinski, *Ber.*, **57**, 2058 (1924); Linstead, Michaelis, and Thomas, *J. Chem. Soc.*, 1139 (1940).

(7) The dehydrogenation, like the isomerization, depends upon concentration; *d*-limonene is completely converted to *p*-cymene by a solution 3.2 Molar in I, but is recovered unchanged from a solution 0.67 Molar in I.

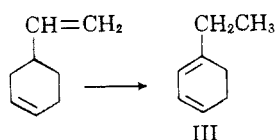
hydrogenate α -phellandrene (conjugated double bonds) to *p*-cymene in the same yield as does I.

Mechanism of the reactions. Although migration of double bonds usually occurs under the influence of acids, there are examples of base-catalyzed rearrangements which are similar to those reactions reported here.⁸ By analogy with the work of Pines, Veseley, and Ipatieff,^{8a} the mechanism of the isomerization in the present case may be written:



This mechanism is inadequate, however, in failing to consider any role of the metal ion. It does not seem likely that the structures of the lithium and sodium compounds are very different, or that the high viscosity of the solution of II would have so great an effect upon the rate of isomerization. Nor is it likely that an essential similarity between the two is masked by solvation effects.⁹ It should be pointed out, however, that certain reactions in which the anion is usually regarded as the active reagent may actually be greatly influenced by the cation present. Brady and Jakobovitz have discussed this problem in some detail,¹⁰ and have offered explanations for several instances where the cation affects the course of the reaction. In the present work, no explanation can as yet be offered, so that the reactions must be discussed from the admittedly incomplete viewpoint which considers only the anion.

It seems reasonable that the first step in the dehydrogenation of 4-vinylcyclohexene is isomerization to the conjugated diene (III or isomer). This



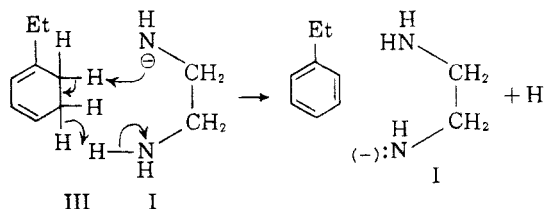
(8) (a) H. Pines, J. A. Veseley, and V. N. Ipatieff, *J. Am. Chem. Soc.*, **77**, 347 (1955); (b) A. A. Morton and E. J. Lanpher, *J. Org. Chem.*, **20**, 839 (1955); (c) T. L. Jacobs, R. Akawie, and R. G. Cooper, *J. Am. Chem. Soc.*, **73**, 1273 (1951).

(9) The initial step in the isomerization as written above involves attack of the amine anion, $(\text{H}_2\text{NCH}_2\text{CH}_2\bar{\text{N}}\text{H})^-$, on the α -carbon of the olefin, with removal of a proton. It is probable that the lithium cation, because of its small size, can be solvated by only one or two solvent molecules; with sodium, the cation is larger, so that it can coordinate several solvent molecules. This difference may, in some manner, decrease the concentration or availability of the $(\text{H}_2\text{NCH}_2\text{CH}_2\bar{\text{N}}\text{H})^-$ ion when sodium is the cation present.

(10) O. L. Brady and J. Jakobovitz, *J. Chem. Soc.*, 767 (1950). See also H. Morita and A. V. Tobolsky, *J. Am. Chem. Soc.*, **79**, 5853 (1957); H. F. Herbrandson and D. S. Mooney, *J. Am. Chem. Soc.*, **79**, 5809 (1957), and references cited therein.

is suggested by the fact that II will not dehydrogenate *d*-limonene (where the bonds must first be isomerized to a conjugated system), but will dehydrogenate α -phellandrene (where the double bonds are already conjugated). Since the first step in either isomerization or dehydrogenation is the removal of a proton from a carbon atom adjacent to a double bond, the reactions depend partly upon the relative acidity of the active hydrogens of the hydrocarbons (or upon the basicity of the resulting carbanion). Both I and II readily remove protons from cyclic conjugated dienes, but the removal of a less acidic proton from an unconjugated diene by II must be a slow process.

The path from III to ethylbenzene remains to be elucidated. In analogy with the isomerization mechanism, the first step may be the formation of a carbanion, which is then transformed to ethylbenzene by loss of a hydride ion. This may take place by elimination of a hydride ion as such, which would then react rapidly with either ethylenediamine or with hydrocarbon III or another molecule of 4-vinylcyclohexene, with formation of the corresponding anion and hydrogen. The bidentate character of ethylenediamine makes it possible to visualize a concerted reaction in which III and I form a cyclic intermediate.



As this mechanism is written, the hydride ion is never free in solution. If it were free, it might be expected to react with other substrates present. When a mixture of *d*-limonene and 4-methylcyclohexene is treated with I, the products are *p*-cymene and 1-methylcyclohexene. No methylcyclohexane is present; thus, hydride ion has not been transferred intermolecularly. This lends some support to the idea of the cyclic intermediate, with no formation of free hydride ion. It should be noted, however, that *N*-lithiotrimethylenediamine, $\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{NHLi}$, is also capable of isomerizing a terminal olefin and dehydrogenating α -phellandrene. Thus, if the dehydrogenation does proceed *via* a cyclic intermediate, the size of the ring formed in the transition state is not critical.

This reaction is of considerable interest in that it is a low temperature, base-catalyzed, homogeneous chemical dehydrogenation which proceeds in very high yield. Pines and co-workers^{8a,11} dehydrogenated *d*-limonene to *p*-cymene by sodium with a promoter such as *o*-chlorotoluene; this reaction is much slower than the lithium-ethylenediamine re-

(11) H. Pines and H. E. Eschinazi, *J. Am. Chem. Soc.*, **77**, 6314 (1955).

action and is carried out at a considerably higher temperature. 2,5-Dihydrotoluene is partly converted to toluene by sodium amide or potassium amide in liquid ammonia¹²; however, this conversion of dihydrotoluene to toluene may take place by a hydrogen transfer (disproportionation) rather than by loss of molecular hydrogen. Furthermore, *d*-limonene is not isomerized or dehydrogenated by these reagents. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone can dehydrogenate tetralin, acenaphthene, and dibenzyl at room temperature¹³; here again, the reaction is a hydrogen transfer. In general, most nonbiological dehydrogenation reactions take place at temperatures above 200°. The dehydrogenation reaction in ethylenediamine, which produces molecular hydrogen and proceeds at a measurable rate even at room temperature, is certainly unusual. It remains to be seen whether other metal derivatives of amines or of ammonia may function in a similar way.

EXPERIMENTAL

Materials. Lithium, obtained from the Lithium Corp. of America, was used in the form of 1/8 inch wire. Anhydrous ethylenediamine (Union Carbide Chemicals Co. and Eastman) was purified by heating with sodium for a day or two, followed by distillation. Trimethylenediamine (American Cyanamid Co.) was heated with sodium for a few hours and then distilled.

Apparatus and procedure. A 4-neck flask, or a 3-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. The apparatus was flushed out with nitrogen, the ethylenediamine added, and the amine heated to 90–110°. The lithium was then added in portions through the straight reflux condenser; 4 to 8 pieces, each about 1.5 inches long, were added in each portion. The rate of addition of the lithium was controlled by the hydrogen evolution and by the persistence of the dark blue color; usually gas evolution was the determining factor, the metal being added during 1.5 to 3 hours without waiting for discharge of the blue color between portions, while the mixture was stirred and maintained at 90–110°. After all of the lithium had been added and the dark blue color had disappeared, the mixture was heated for 1 or 2 hr. at 90–100° in order to be certain that all of the metal had reacted. (The final solution varied from colorless to a pale yellow or tan; it usually contained a small amount of white solid in suspension. If this colorless solution were exposed to air, a blue color formed, which was slowly destroyed when the solution was heated for a time. This color, however, was much lighter than the blue of the dissolving lithium.) The compound to be isomerized was then added at a temperature of 90–100° and the mixture stirred and heated for 1 to 5 hr. (In the dehydrogenations, the hydrocarbon was added slowly, because of the vigorous gas evolution.) The flask was then cooled in ice, and water added until most of the solid which first formed had dissolved. The product was then isolated in the usual manner and analyzed, usually by infrared spectroscopy.

Isomerization experiments. 1-Octene. (a) To a solution of *N*-lithioethylenediamine (I), prepared from 11.10 g. (1.60

moles) of lithium and 375 ml. of ethylenediamine, there was added 44.8 g. (0.40 mole) of 1-octene. The mixture was refluxed gently for 2.25 hr. The product (90.1% yield) consisted of internal olefins. The infrared spectrum indicated that the product was mainly 2-octene, in the proportion of approximately 60% *trans* to 40% *cis*; 1-octene was absent.

(b) To a solution of I prepared from 0.416 g. (0.06 mole) of lithium and 180 ml. of ethylenediamine, there was added 33.6 g. (0.30 mole) of 1-octene. The mixture was refluxed gently for 4.25 hr. The product consisted entirely of 1-octene; no β -olefin was present.

(c) A mixture of 375 ml. of ethylenediamine and 44.8 g. (0.40 mole) of 1-octene was refluxed gently for 5.75 hr. The product consisted entirely of unchanged 1-octene.

(d) A solution of H₂NCH₂CH₂NHNa (II) was prepared from 13.8 (0.60 mole) of sodium and 187 ml. of ethylenediamine by heating for 9 hr.; the reaction is much slower with sodium than it is with lithium. To the resulting dark brown viscous solution there was added 44.8 g. (0.40 mole) of 1-octene during 1 hr., while maintaining the solution at about 100°. The mixture was heated for 6 hr. and then worked up in the usual manner. The product consisted largely of unchanged 1-octene, but some isomerization to internal octenes had taken place. The yield of internal olefins, corrected for a small amount present in the starting material, was 2.2%. No octane was present. There was also obtained a fairly large amount of white solid, insoluble in water and insoluble in the organic layer, which was readily removed by filtration.

(e) To a solution of *N*-lithiotrimethylenediamine, H₂N-CH₂CH₂CH₂NHLi, prepared from 1.78 g. (0.26 mole) of lithium and 60 ml. of trimethylenediamine, there was added 7.17 g. (0.064 mole) of 1-octene. The mixture was stirred and heated for 2 hr. at 100–108°. The product consisted entirely of internal olefins.

4-Methylcyclohexene. To a solution of (I) prepared from 8.33 g. (1.20 moles) of lithium and 187 ml. of ethylenediamine, there was added 19.2 g. (0.20 mole) of 4-methylcyclohexene. The mixture was heated for 2 hr. The product consisted largely of 1-methylcyclohexene, but some starting material was still present. Toluene was absent.

Dehydrogenation experiments. *d*-Limonene. (a) To a solution of I prepared from 16.65 g. (2.40 moles) of lithium and 375 ml. of ethylenediamine, there was added 54.4 g. (0.40 mole) of *d*-limonene (1-methyl-4-isopropenylcyclohexene) while the solution was maintained at 100–110°. Gas was evolved vigorously during the addition. The mixture was refluxed gently for 2.5 hr. The product (48.42 g., boiling point 167–171°) was pure *p*-cymene. The yield was 90.4%.

(b) To a solution of I prepared from 16.65 g. (2.40 moles) of lithium and 375 ml. of ethylenediamine, there was added during 1 hr. 54.4 g. (0.40 mole) of *d*-limonene. The solution was maintained at room temperature throughout the addition. After stirring for 0.5 hr., the mixture was decomposed with water, the temperature being maintained below 20°. The yield of *p*-cymene was 3.6%; the balance of the material was mostly *d*-limonene, but some isomers of *d*-limonene may have been present.

(c) To a solution of I prepared from 4.17 g. (0.60 mole) of lithium and 187 ml. of ethylenediamine, there was added 27.2 g. (0.20 mole) of *d*-limonene. Gas was evolved vigorously during the addition. The mixture was heated for 4.5 hr. The product consisted of *p*-cymene; the yield was 98.1%.

(d) A solution of H₂NCH₂CH₂NHNa was prepared by dissolving 13.8 g. (0.60 mole) of sodium (6–8 millimeter shot) in 187 ml. of ethylenediamine. *d*-Limonene (27.2 g., 0.20 mole) was then added and the mixture heated for 9 hr. No gas was evolved. The mixture was worked up in the usual way; some brown solid material which was present was not investigated. There was obtained an 87.9% recovery of *d*-limonene; no *p*-cymene was present.

(e) To a solution of I prepared from 13.88 g. (2.00 moles) of lithium and 375 ml. of ethylenediamine, there was added

(12) A. J. Birch, *J. Chem. Soc.*, 1642 (1947).

(13) E. A. Braude, A. G. Brook, and R. P. Linstead, *J. Chem. Soc.*, 3569 (1954).

272 g. (2.00 moles) of *d*-limonene during 1.5 hr. The mixture was heated for 0.5 hr. The product (250.5 g., b.p. 170–173°) consisted entirely of *p*-cymene; the yield was 92.1%.

(f) To a solution of I prepared from 1.74 g. (0.25 mole) of lithium and 375 ml. of ethylenediamine, there was added 136 g. (1.00 mole) of *d*-limonene. The mixture was heated for 1 hr.; no gas was evolved. The product consisted entirely of *d*-limonene (124.8 g., b.p. 169–172°; 91.7% recovery).

4-Vinylcyclohexene. To a solution of I prepared from 8.33 g. (1.20 moles) of lithium and 187 ml. of ethylenediamine there was added during 0.5 hr. 21.6 g. (0.20 mole) of 4-vinylcyclohexene; gas was evolved vigorously. Heating was continued for another 2.75 hr.; during this time gas evolution continued at the rate of about 1 l. per hr. The product consisted entirely of ethylbenzene; yield 86.8%.

α-Phellandrene. (a) To a solution of I prepared from 8.33 g. (1.20 moles) of lithium and 187 ml. of ethylenediamine, there was added 27.2 g. (0.20 mole) of crude 2-methyl-5-isopropyl-1,3-cyclohexadiene (*α*-phellandrene, containing about 20% *p*-cymene). Gas was evolved vigorously. The mixture was heated for 1 hr. The product consisted entirely of *p*-cymene; the yield (corrected for *p*-cymene in the starting material) was 73.7%.

(b) To a solution of $H_2NCH_2CH_2NHNa$ prepared by dissolving 13.8 g. (0.60 mole) of sodium shot in 187 ml. of ethylenediamine, there was added 27.2 g. (0.20 mole) of crude *α*-phellandrene. The mixture was then heated for 4.5 hr. The product consisted entirely of *p*-cymene; the yield (corrected for *p*-cymene in the starting material) was 76.1%.

There was also obtained a white solid, insoluble in both the aqueous and organic phases.

(c) A mixture of 27.2 g. (0.20 mole) of crude *α*-phellandrene and 190 ml. of ethylenediamine was heated at 100° for 1 hr. The product, obtained in 87.2% yield, consisted of unchanged *α*-phellandrene.

(d) To a solution of $H_2NCH_2CH_2CH_2NHLi$, prepared from 2.67 g. (0.39 mole) of lithium and 60 ml. of trimethylenediamine, there was added 6.73 g. (0.064 mole) of crude *α*-phellandrene. The mixture was stirred and heated for 2 hr. at 112°. The product (5.33 g.) contained about 80% of *p*-cymene and 7.5% of *α*-phellandrene. The yield of *p*-cymene (corrected for *p*-cymene in the starting material) was 40%.

Limonene and 4-methylcyclohexene. To a solution of I prepared from 8.33 g. (1.20 moles) of lithium and 375 ml. of ethylenediamine, there was added a mixture of 54.4 g. (0.40 mole) of *d*-limonene and 76.8 g. (0.80 mole) of 4-methylcyclohexene. Gas was evolved vigorously during the addition. The mixture was heated for 4 hr. The products and yields (mass spectrometric analyses) were: *d*-limonene, 2.5%; *p*-cymene, 87.8%; 4-methylcyclohexene, 24.1%; 1-methylcyclohexene, 63.4%. Methylcyclohexane was probably absent, but may have been formed in a yield not exceeding 0.1%.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE VIRGINIA POLYTECHNIC INSTITUTE]

Synthesis of Some Trichloromethyl-2-benzylphenylcarbinols^{1,2}

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A series of new trichloromethyl-2-benzylphenylcarbinols, which can be considered as synthetic precursors of the DDT-type molecule, have been prepared by several reaction sequences. From the toxicity data against German cockroaches it would appear that the compounds tested have little if any insecticidal activity. Many intermediates were also tested.

In connection with our studies on the mechanism of insecticidal action of DDT, 2,2,2-trichloro-1,1-bis(*p*-chlorophenyl)ethane, we have synthesized a series of trichloromethyl-2-benzylphenylcarbinols (IVa-IVd) which are synthetic precursors of the DDT-type molecule. Since many carbinols³ of diversified structure have been synthesized and tested for insecticidal activity, we thought compounds of the type IV would be especially interesting for several reasons.

First, Fisher-Hirschfelder-Taylor models of compounds of the type IV indicate that free rotation of one phenyl group is not possible and that free rotation of the other phenyl group is severely hindered

so that the trihedralized⁴ configuration may be realized. Rogers, Brown, Rasmussen, and Heal⁴ have pointed out the importance of a trihedralized *p,p'*-dichlorophenyl moiety in explaining the toxicity of DDT.

Second, compound IVd has other important structural features in common with DDT; namely, a trichloromethyl group and two *p*-chlorophenyl groups whose chlorine atoms are about as distant as those in DDT.

Third, compounds of the type IV are known³ to exhibit narrow-spectrum insecticidal properties and are thus ideally suited for activity-structure studies with certain insects.

Ketones Ia and Ib are prepared in excellent yield

(1) Presented before the Division of Organic Chemistry at the 132nd Meeting of the American Chemical Society, New York, N. Y., September 1957.

(2) This paper has been abstracted from the master's thesis of G. J. Buese and the doctorate thesis of P. E. Newallis presented to the Virginia Polytechnic Institute in 1951 and 1957, respectively.

(3) R. C. Blinn, F. A. Gunther, and R. L. Metcalf, *J. Am. Chem. Soc.*, **76**, 37 (1954) and references listed there.

(4) E. F. Rogers, H. D. Brown, I. M. Rasmussen, and R. E. Heal, *J. Am. Chem. Soc.*, **75**, 2991 (1953). According to these authors the concept of trihedralization may be generalized as follows: "In compounds having one carbon atom two or three planar groups and a group sufficiently large to hinder the rotation of the planar groups, although capable of rotation itself, the planar groups will tend to positions corresponding to the sides of a trihedral angle."