and the same procedure followed. Time of reduction was noted and compared with the standard experiment. In addition, half a molecular equivalent was used in experiments with hydrochloric, oxalic, cyclohexylsulfamic acids in the strong acid group, and with acetic, tartaric, and succinic acids in the milder acid group and the effects noted.

In order to determine whether hydrogen uptake was complete, the solution, after reduction, was filtered from the catalyst and concentrated. If acid was not used in the reduction, the residue was dissolved in dry chloroform and made up to 50 cc. with that solvent. A sample of the solution was submitted for infrared analysis and comparison with known standards of benzylbutylamine and benzylidenebutylamine.[9] When the procedure using acid was followed, the residue obtained after work up was treated with water and excess sodium hydroxide. The base was then extracted with benzene and the extract dried over anhydrous magnesium sulfate. After filtration and removal of solvent the residue was dissolved in chloroform and made to 50 cc. total volume. A sample was then submitted for infrared examination.

Effect of acids on reduction of toluene or benzoic acid. Toluene or benzoic acid (0.1 mole) in 100 cc. of analytical reagent methyl alcohol was hydrogenated in the presence of 20% by weight of 5% rhodium on alumina (or 5% rhodium on carbon) under 2 atm. pressure. Uptake of hydrogen was complete in 90 min. In similar reductions in the presence of 0.1 mole of III or IV no change in time was noted. However, with either toluene or benzoic acid and 0.1 mole of hydrochloric acid uptake of hydrogen was only 25% of $3H_2$ in 6 hr.

NORTH CHICAGO, ILL.

---

(9) Carried out by W. Washburn of Abbott Laboratories.

[CONTRIBUTION FROM THE UNITED STATES DEPARTMENT OF THE INTERIOR, BUREAU OF MINES, REGION V]

The Lithium-Ethylenediamine System. III. Formation of Imidazole Derivatives and Cleavage of Certain Carbon-Carbon Bonds[1]

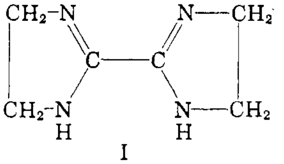
LESLIE REGGEL,[2] JOSEPH P. HENRY,[3] AND IRVING WENDER[2]

Received June 27, 1960

Hydrocarbons such as tetralin and isopropylbenzene, in the presence of *N*-lithioethylenediamine, $H_2NCH_2CH_2NHLi$ catalyze the self-condensation of ethylenediamine to give bis(Δ^2-2-imidazolinyl), hydrogen, and ammonia. In the presence of *N*-sodioethylenediamine, $H_2NCH_2CH_2NHNa$, a similar reaction takes place and in addition yields an unidentified compound, $C_6H_8N_4$. Stilbene with *N*-lithioethylenediamine gives bis(Δ^2-2-imidazoinyl), toluene, and 1,2-diphenylethane; under the same conditions, 1,2-diphenylethane is unchanged.

We have shown[1] that reaction of certain dienes, such as *d*-limonene, with *N*-lithioethylenediamine, $H_2NCH_2CH_2NHLi$ (NLA), leads to the evolution of hydrogen and the formation of the corresponding aromatic hydrocarbon. This paper describes experiments designed to extend the scope of the dehydrogenation reaction.

When tetralin was heated at 90–100° with *N*-lithioethylenediamine in solution in excess ethylenediamine, there was a slow evolution of hydrogen and ammonia. Only one organic product, other than recovered tetralin, was isolated from the mixture; it was identified as bis(Δ^2-2-imidazolinyl), I.[4] Similar results were obtained when toluene, ethylbenzene, or isopropylbenzene was used in place of tetralin.[5] The formation of I appeared to be fastest with tetralin and slowest with toluene. In one experiment with tetralin, the rate of gas evolution at the end of eighty-three hours of intermittent heating was approximately the same as at the start.



I

Woodburn and O'Gee[4] obtained I from the reaction of ethylenediamine with cyanogen at 0°. The over-all reaction can be written:

$$C_2N_2 + 2\ C_2H_8N_2 \longrightarrow C_6H_{10}N_4 + 2\ NH_3 \qquad (1)$$

In the present work, the over-all reaction seems to be:

$$3\ C_2H_8N_2 \longrightarrow C_6H_{10}N_4 + 2\ NH_3 + 4\ H_2 \qquad (2)$$

The dehydrogenation of ethylenediamine to cyanogen by *N*-lithioethylenediamine does not seem likely; nor would this pathway explain the need for the aromatic hydrocarbon. It is more likely that some reaction occurs which produces various intermediate compounds, and that the aromatic hydrocarbon, perhaps in the form of some metallated derivative, plays a part. The relative proportions of

---

[1] For the previous paper, see L. Reggel, S. Friedman, and I. Wender, *J. Org. Chem.*, **23**, 1136 (1958). A portion of the material in the present paper was presented before the Division of Organic Chemistry at the 129th Meeting, American Chemical Society, Dallas, Tex., April 1956.

[2] Bureau of Mines, U.S. Department of the Interior, Pittsburgh, Pa.

[3] Union Carbide Corp., South Charleston, W. Va. This work was carried out as part of a cooperative agreement between the Bureau of Mines and the Union Carbide Corp.

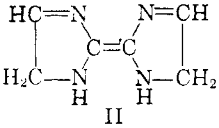
[4] H. M. Woodburn and R. C. O'Gee, *J. Org. Chem.*, **17**, 1235 (1952). We wish to thank Dr. Woodburn for supplying a sample of this material.

[5] In the presence of decalin, a very small amount of I was formed; this may have arisen from a trace amount of tetralin in the decalin.

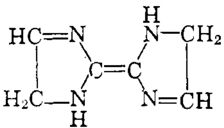
ammonia and hydrogen predicted by Equation 2, 33% ammonia and 67% hydrogen, are close to the approximate values found experimentally (30% ammonia and 70% hydrogen). No evidence was found for the presence of any compound intermediate between ethylenediamine and I; if any were formed, they would probably be water-soluble and difficult to detect in the presence of an excess of water and ethylenediamine.

The formation of I from a hydrocarbon, ethylenediamine, and *N*-sodioethylenediamine, $H_2NCH_2CH_2NHNa$ (NSA), was next investigated. When α-phellandrene was heated with *N*-sodioethylenediamine in ethylenediamine, hydrogen was evolved and *p*-cymene and I were formed.[1] However, when either 1-octene or isopropylbenzene was heated with *N*-sodioethylenediamine, the I obtained was not pure, but was contaminated by another substance. This new material was isolated by taking advantage of the rapid hydrolysis of I by hot water to water-soluble products. The other component of the mixture (hereafter called the dehydro compound) was insoluble in cold water and was readily obtained pure.[6]

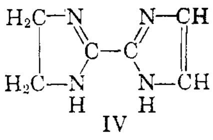
The exact structure of the dehydro compound had not been determined. Analysis gave the empirical formula $C_6H_8N_4$, with a calculated molecular weight of 136. The molecular weight was determined by low ionizing voltage mass spectrometry and the exact value of 136 was found. For comparison, a molecular weight determination was made on I; the value found, 138, corresponded exactly to the theoretical. The infrared and ultraviolet spectra of the dehydro compound did not lead to any definite decision on its structure. On the assumption that it contains three conjugated double bonds,[7] three possible structures can be written:



II



III



IV

An attempt to distinguish between IV and the *cis-trans* pair II and III by means of NMR was unsuccessful because of the very low solubility of the dehydro compound in the solvents used (water, methanol, dimethylformamide, carbon tetrachloride). The location of the three positions of unsaturation in the dehydro compound must be left open. We favor II and III rather than IV; the latter contains one ring with the same structure as that of I and might be expected to undergo the same ready hydrolysis.

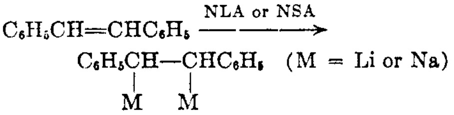
The dehydro compound reacted with both benzoyl chloride and *p*-toluyl chloride to give solid derivatives. An attempt to convert I and the dehydro compound to the same perhydro structure failed; the dehydro compound was not reduced.

Another series of experiments with *N*-lithioethylenediamine began with the treatment of *cis*-stilbene with *N*-lithioethylenediamine. It was hoped that dehydrogenation of *cis*-stilbene to phenanthrene might occur. However, the materials formed were 1,2-diphenylethane, toluene, and I; no phenanthrene, *cis*-stilbene, or benzene could be detected. In addition, there was formed a considerable amount of another solid; its properties suggested that it was an amine hydrochloride, but attempts to purify it were unsuccessful and it was not identified nor analyzed. Under the same conditions, *trans*-stilbene with *N*-lithioethylenediamine gave 1,2-diphenylethane, toluene, a small amount of recovered starting material, I, and a solid probably identical with that obtained with *cis*-stilbene. Similarly, *trans*-stilbene with *N*-sodioethylenediamine gave 1,2-diphenylethane, toluene, a small amount of recovered starting materials, I, and the dehydro compound.

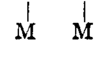
Diphenylacetylene with *N*-lithioethylenediamine gave 1,2-diphenylethane, toluene, and a small amount of recovered starting material; no nitrogen-containing materials were isolated. 1,4-Diphenylbutadiene with *N*-lithioethylenediamine gave largely polymeric material; toluene and I were also formed, but there was no indication of the presence of 1,4-diphenylbutane. Benzhydrol did not react with *N*-lithioethylenediamine, no formation of diphenylmethane or of I being observed.

The formation of both toluene and 1,2-diphenylethane from either *N*-lithioethylenediamine or *N*-sodioethylenediamine and stilbene suggests that the reaction may consist of the steps:

$$H_2NCH_2CH_2NH_2 \xrightarrow{\text{NLA or NSA + hydrocarbon}} H_2 + NH_3 + \text{I} \qquad (3)$$



$$C_6H_5CH{=}CHC_6H_5 \xrightarrow{\text{NLA or NSA}} \underset{\textstyle M}{C_6H_5CH}{-}\underset{\textstyle M}{CHC_6H_5} \quad (M = \text{Li or Na}) \qquad (4)$$

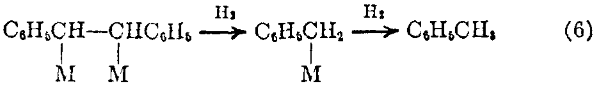


$$\underset{\textstyle M}{C_6H_5CH}{-}\underset{\textstyle M}{CHC_6H_5} \xrightarrow{H_2} C_6H_5CH_2CH_2C_6H_5 \qquad (5)$$

---

[6] It should be noted that although α-phellandrene is converted to *p*-cymene by either *N*-lithioethylenediamine or *N*-sodioethylenediamine, the formation of I is observed only when α-phellandrene is treated with *N*-sodioethylenediamine; this difference may be due to a rate factor. 1-Octene with *N*-lithioethylenediamine is isomerized to 2-octene, but there is no formation of I. However, either 1-octene or 2-octene with *N*-sodioethylenediamine gives both I and the dehydro compound. It is apparent that *N*-sodioethylenediamine is a better reagent than *N*-lithioethylenediamine for the formation of the heterocyclic nitrogen compounds.

[7] Structures in which the three double bonds are not conjugated, or are cross-conjugated, seem less likely, since the compound is formed in the presence of a reagent which readily shifts double bonds.



$$\underset{M}{C_6H_5CH}-\underset{M}{CHC_6H_5} \xrightarrow{H_2} \underset{M}{C_6H_5CH_2} \xrightarrow{H_2} C_6H_5CH_3 \qquad (6)$$

When 1,2-diphenylethane was heated with N-lithioethylenediamine, it was recovered unchanged (93% yield) and neither toluene nor I was found. Evidently reaction (3) proceeds rapidly in the presence of stilbene, producing hydrogen which is partly used up in reactions (5) and (6); whereas reaction (3) does not take place at an appreciable rate when the hydrocarbon present is 1,2-diphenylethane. When a mixture of 1,2-diphenylethane and isopropylbenzene was heated with N-lithioethylenediamine, the starting materials were recovered; no toluene was found. Even in this experiment, where some I was formed, the hydrogen evolved was not used to cleave the diphenylethane. This would seem to substantiate the idea that the cleavage reaction leading to toluene does not take place directly via stilbene, but through some intermediate such as suggested above.

EXPERIMENTAL[8]

In the following experiments, N-lithoethylenediamine was prepared from 8.33 g. (1.20 moles) of lithium (one-eighth inch wire, obtained from the Lithium Corp. of America) and 187 ml. of ethylenediamine. N-Sodioethylenediamine was prepared from 13.8 g. (0.60 mole) of sodium (6–8 mm. shot) and 187 ml. of ethylenediamine. The procedures followed, and the purification of the ethylenediamine (obtained from the Union Carbide Corp.) have been described.[1]

Tetralin (15.5 g., 0.117 mole) was added to a solution of N-lithioethylenediamine and the mixture stirred and heated intermittently at 90–100° for a total of 83 hr. Gas evolution was not measured accurately, but approximated 200 to 1000 ml. per hr.; it ceased when the mixture was allowed to cool, but resumed the next day as soon as the temperature reached about 90°. The reaction mixture became thick. At the end of the heating period, the flask was cooled, and water was added slowly, followed by ether. The ether layer was separated and the aqueous layer, which contained a large amount of insoluble white solid in suspension, was extracted once with ether. The combined ether layers were washed with dilute hydrochloric acid, dried, and distilled; there was obtained 12.55 g. (81%) of tetralin. The aqueous layer was filtered and the solid air-dried, giving 22 g. of material. Recrystallization from absolute alcohol gave 11.46 g. of long flat white crystals. The mother liquors yielded three additional crops, making the total yield 14.08 g. The compound decomposed slowly around 300° without melting. A portion of the first crop was recrystallized twice from absolute alcohol.

Anal. Calcd. for $C_6H_{10}N_4$: C, 52.15; H, 7.30; N, 40.55. Found: C, 52.10; H, 7.20; N, 40.58.

The molecular weight was determined by introducing a saturated ethanol solution into a Consolidated Electrodynamics Model 103-B mass spectrometer. The heated inlet was operated at 285°; the ionizing voltage was approximately 12 volts. The molecular weight found, 138, corresponded exactly to the theoretical value. The infrared spectrum was identical with that of a sample of bis(Δ^2-2-imidazolinyl) kindly supplied by Dr. H. M. Woodburn.[4]

In another experiment, 5 g. (0.038 mole) of tetralin was heated for a total of 89 hr. with a solution of N-lithioethylenediamine. A total of 14.60 g. of I was obtained. The gas which was evolved consisted of 70% hydrogen and 30% ammonia (mass spectrometric analysis).

Toluene (27.6 g., 0.30 mole) was heated with a solution of N-lithioethylenediamine at 100° for 69 hr. Gas evolution was very slow. There was obtained 2.42 g. of I.

Ethylbenzene (10.00 g., 0.0944 mole) was heated with a solution of N-lithioethylenediamine for 53 hr. The gas which was slowly evolved consisted of 16–19% ammonia and 81–84% hydrogen. There was obtained 5.67 g. of I.

Isopropylbenzene (11.32 g., 0.0944 mole) was heated with a solution of N-lithioethylenediamine for 11 hr. Hydrogen and ammonia were evolved. The mixture was not worked up for I.

cis-Stilbene (18.00 g., 0.10 mole) was added to a solution of N-lithioethylenediamine at 105–110°. The solution became deep red; gas was evolved rapidly for a few minutes. The mixture was stirred and heated at 105–110° for 2 hr.; during this time gas evolution continued at a very slow rate. The mixture was cooled and water added, followed by ether. A small amount of I was filtered off. The ether layer was washed with dilute hydrochloric acid; a white precipitate formed and was filtered off. The ether layer was washed again with dilute hydrochloric acid, dried, and distilled. Analysis of the fractions by infrared and mass spectrometric methods showed the products and yields to be: toluene, 1.05 g., 5.7%; 1,2-diphenylethane, 3.37 g., 18.5%; stilbene, absent; benzene, absent.

The insoluble white material (see above) was air-dried for several days; it turned pale violet. The material was quite recalcitrant; it contained nitrogen and chlorine and appeared to be an amine hydrochloride, but its properties were not improved by recrystallization or attempted formation of a benzoyl derivative. The infrared and ultraviolet spectra yielded no useful information.

In another experiment in which *cis*-stilbene was heated with N-lithioethylenediamine for 2.5 hr. at 106–109°, the products were: I, 0.48 g.; toluene, 1.73 g., 9.8%; 1,2-diphenylethane, 2.54 g., 14.5%; stilbene, absent; benzene, absent.

trans-Stilbene (18.00 g., 0.10 mole) was added to a solution of N-lithioethylenediamine. The mixture was heated for 4.5 hr. and then worked up as described above for *cis*-stilbene. The products were: toluene, 2.53 g., 13.8%; *trans*-stilbene, 0.04 g., 0.2%; 1,2-diphenylethane, 3.12 g., 17.1%; I, 0.21 g.; white solid (turning pale violet after exposure to air), insoluble in both ether and dilute hydrochloric acid, *ca.* 6.7 g. Two grams of this material was refluxed with 100 ml. of 1:4 sulfuric acid for 4 hr. The resulting deep maroon solid was recrystallized twice from toluene, giving 0.30 g. of tiny maroon needles.

Anal. Found: C, 79.56; H, 5.20; N, 3.62, 3.42; ash, 3.90.

The infrared spectrum gave no useful information; the ultraviolet spectrum indicated a long conjugated system.

Diphenylacetylene (17.8 g., 0.10 mole) was dissolved in 100 ml. of ethylenediamine and added during 15 min. to a solution of N-lithioethylenediamine. The solution turned very dark at once. The mixture was stirred and heated for 40 min. at 85–100°, allowed to stand for 64 hr. and then heated for 2 hr. at 100–105°. After the usual treatment there was obtained: toluene, 1.25 g., 6.8%; diphenylacetylene, 0.06 g., 0.3% recovery; 1,2-diphenylethane, 1.10 g., 6.1%. The 1,2-diphenylethane was contaminated with an unknown amount of a material of molecular weight 196 (mass spectrometer); this corresponds to a methyl derivative of diphenylethane. There was no indication of the formation of I or of any other water- and ether-insoluble compounds.

1,2-Diphenylethane (18.2 g., 0.10 mole) was added to a solution of N-lithioethylenediamine. The mixture was heated 1.5 hr.; it turned green, then purple, then dark green, and finally colorless. 1,2-Diphenylethane was recovered (17.05 g., 93.7%). Neither toluene nor I was found.

---

(8) Analyses by Galbraith Microanalytical Laboratories, Knoxville, Tenn., and by Huffman Microanalytical Laboratories, Wheatridge, Colo.

A mixture of 1,2-diphenylethane (18.2 g., 0.10 mole) and isopropylbenzene (11.8 g., 0.098 mole) was heated at 95° with a solution of *N*-lithioethylenediamine for 35 hr. No toluene was formed; starting materials were recovered. I, 0.87 g., was also formed.

1,4-Diphenyl-1,3-butadiene (20.5 g., 0.10 mole) was heated with a solution of *N*-lithioethylenediamine at 117° for 2.5 hr. The gas which was evolved consisted of ammonia (60%) and hydrogen (39%). The reaction mixture gave 1.32 g. of I and 1.59 g. (8.6%) of toluene. The remainder of the diphenylbutadiene was converted into dark nondistillable material which appeared to be polymeric. No evidence for the presence of diphenylbutane was obtained.

trans-Stilbene (18.0 g., 0.10 mole) was added to a solution of *N*-sodioethylenediamine and the mixture heated for 4.5 hr. at 101–102°. There was obtained 0.069 g. (0.4%) of toluene and 1.26 g. (6.9%) of 1,2-diphenylethane; a large amount of *trans*-stilbene was recovered. The water- and ether-insoluble fraction (5.2 g.) was a mixture of I and the dehydro compound.

α-Phellandrene (2-methyl-5-isopropyl-1,3-cyclohexadiene, 27.2 g., 0.20 mole) was heated with a solution of *N*-sodioethylenediamine for 4.5 hr. There was obtained a 76.1% yield of *p*-cymene and 9.28 g. of I. (The α-phellandrene used contained 20% *p*-cymene; the yield of *p*-cymene has been corrected for the amount present in the starting material.)

1-Octene (44.8 g., 0.40 mole) was heated at 100° with a solution of *N*-sodioethylenediamine for 6.0 hr. Gas was evolved slowly; it contained hydrogen and ammonia. The 1-octene was partly isomerized (*ca.* 2.2%) to internal octenes; 8.3 g. of a mixture of I and the dehydro compound was also obtained.

Isopropylbenzene (24.0 g., 0.20 mole) was heated with a solution of *N*-sodioethylenediamine for 5.25 hr. The flask was cooled, and water and then benzene added. The mixture was filtered to remove the pale cream-colored, pasty solid, which was washed with benzene and with water. The organic layer contained only isopropylbenzene (*ca.* 62% recovery) and benzene. The solid (crude dehydro compound) weighed 14.50 g. after drying in air. It decomposed slowly between 220° and 240° without melting.

The infrared spectrum of the crude dehydro compound as obtained in this and in a previous experiment showed that a hitherto unidentified substance was present, but that it was contaminated with I. Because of the low solubility of I in benzene, an attempt was made to separate the two by extraction with benzene in a Soxhlet extractor. The benzene-soluble portion was then recrystallized twice from absolute alcohol. While the analytical results seemed to indicate that the unknown was a compound containing two less hydrogen atoms than I, the infrared spectrum still contained the main bands of the latter substance. Finally, advantage was taken of the rapid hydrolysis of I to ethylenediamine and oxalic acid. One gram of the crude dehydro compound was heated with water; the entire material dissolved before the solution reached reflux temperature. The solution was refluxed for 15 min. and then cooled; the resulting crystals were recrystallized from absolute alcohol, giving 0.38 g. of material. The infrared spectrum of this was free of the main bands attributed to I. For analysis, the material was twice recrystallized from absolute alcohol, giving almost colorless needles, m.p. 251.0–252.5° (sealed tube).

Anal. Calcd. for $C_6H_8N_4$: C, 52.93; H, 5.92; N, 41.15; mol. wt., 136. Found: C, 52.90; H, 5.95; N, 40.78; mol. wt. (see above), 136.

The dibenzoyl derivative was prepared from 0.30 g. of the dehydro compound, 0.8 ml. of distilled benzoyl chloride, and 10 ml. of dry pyridine, heated on a water bath for 1.5 hr. The product was poured into aqueous sodium carbonate and the solid filtered. Crystallization from benzene-ethanol gave 0.60 g. of white needles, m.p. 221–222.5° with previous sintering. Recrystallization gave 0.49 g. of material, m.p. 222.5–223.5° (sintering from 220°).

Anal. Calcd. for $C_{20}H_{16}N_4O_2$: C, 69.75; H, 4.68; N, 16.27. Found: C, 70.06; H, 4.88; 16.31.

The bis(*p*-toluyl) derivative was prepared in the same way from *p*-toluyl chloride. Two crystallizations from benzene-ethanol gave pale tan needles, m.p. 245.0–248.0°.

Anal. Calcd. for $C_{22}H_{20}N_4O_2$: C, 70.95; H, 5.41; N, 15.05. Found: C, 71.02; H, 5.36; N, 15.04.

Treatment of the dehydro compound (0.50 g.) with hydrogen (1900 p.s.i. at room temperature) for 5 hr. at 200° in the presence of platinum oxide (0.50 g.) and ethanol (90 ml.) gave unchanged starting material. Similar treatment of I resulted in reaction; the products were not identified but it is likely that the molecule was cleaved to give ethylenediamine.

Benzhydrol (18.4 g., 0.10 mole) was heated with a solution of *N*-lithioethylenediamine at 100–115° for 2.5 hr. No gas was evolved. The recovered material consisted only of benzhydrol (71.3%). No evidence for the formation of any other products was obtained.

cis-Decalin (27.6 g., 0.20 mole) was heated with a solution of *N*-lithioethylenediamine for 2.0 hr. The product (21.0 g., 76.0% yield) consisted of *cis*-decalin; none of the *trans* isomer was present.

A *cis-trans* decalin mixture (47% *cis* and 52% *trans* by infrared analysis, with a trace of tetralin; 41.4 g., 0.30 mole) was heated with a solution of *N*-lithioethylenediamine at 100–105° for a total of 37 hr. during a 10-day period. The product (32.3 g., 78.0% recovery) was unchanged in composition; 0.30 g. of I was formed.

Acknowledgment. We wish to thank R. A. Friedel and A. G. Sharkey, Jr., for the spectrometric analyses.

PITTSBURGH 13, PA.