



The synthesis of 2-methyl butanal by reaction of n-butyl isocyanide with secondary-butylcadmium bromide, pt. 1 : a study of the reactions between carbon monoxide and the sodium salt of nitroethane, pt. 2

by John M Bruce Jr

A THESIS Submitted to the Graduate Committee in partial fulfillment of the requirements for the degree of Master of Science in Chemistry at Montana State College

Montana State University

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Abstract:

Part I.

2-methyl butanal was prepared by the following sequence of reactions: [Formulas not Captured by OCR] A light yellow liquid was obtained as product. Confirmatory tests were run using small portions of the final product, and close agreement was found to exist between these results and the actual data pertaining to 2-methyl butanal. The 2,4-dinitrophenylhydrazone derivative was prepared from the final product, and its melting point determined.

Experimental details of the above procedure were presented, along with an explanation of the experimental results.

Part II A reaction mixture consisting of the sodium salt of nitroethane and nickel carbonyl in a solvent of cyclohexane, was subjected to high pressures of carbon monoxide. This reaction mixture yielded, upon hydrolysis, a substance possessing a solubility which could not readily be accounted for. This substance is not obtained in the absence of nickel carbonyl, or when cyclohexane itself is subjected to carbon monoxide under pressure in the presence of nickel carbonyl. The unidentified substance is decomposed by steam distillation, simple distillation, and vacuum distillation, and cannot be crystallized satisfactorily even at low temperatures. Positive Schiff's and Tollen's tests were obtained by use of the appropriate reagent and the unknown substance. Derivatization of the unidentified material has not been possible.

Additional investigation of the unidentified substance is being conducted.

Part I. THE SYNTHESIS OF 2-METHYL BUTANAL BY REACTION OF n-BUTYL ISO-CYANIDE WITH SECONDARY-BUTYLCADMIUM BROMIDE.

Part II. A STUDY OF THE REACTIONS BETWEEN CARBON MONOXIDE AND THE SODIUM SALT OF NITROETHANE.

By

JOHN M. BRUCE, Jr.

A THESIS

Submitted to the Graduate Committee

in

partial fulfillment of the requirements

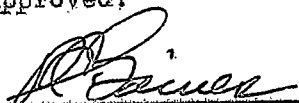
for the degree of

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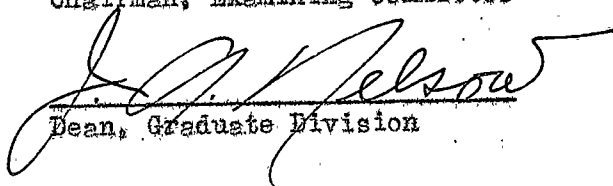
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Chairman, Examining Committee


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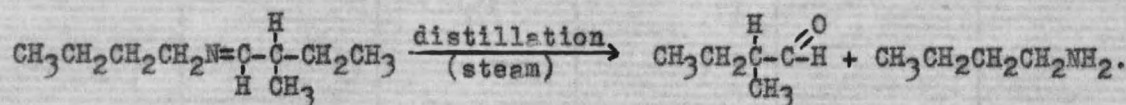
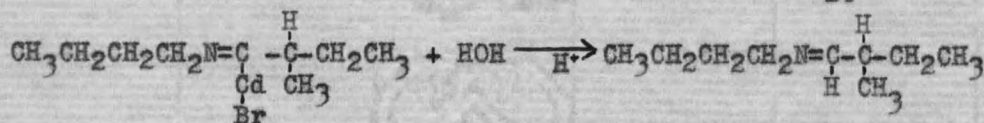
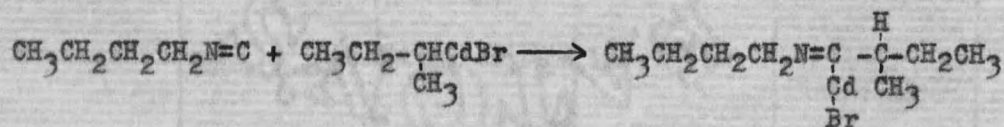
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I. ABSTRACT

Part I.

2-methyl butanal was prepared by the following sequence of reactions:



A light yellow liquid was obtained as product. Confirmatory tests were run using small portions of the final product, and close agreement was found to exist between these results and the actual data pertaining to 2-methyl butanal. The 2,4-dinitrophenylhydrazone derivative was prepared from the final product, and its melting point determined.

Experimental details of the above procedure are presented, along with an explanation of the experimental results.

II. INTRODUCTION

The isocyanides, or carbylamines, RNC , exist as colorless liquids, which are insoluble in water, and have a particularly disagreeable odor. The vapors are very toxic, capable of causing dizziness and vomiting if inhaled over a sufficient period of time.

The carbylamines are very reactive compounds. Some general reactions involving isocyanides and other molecules are listed by Nef⁽²⁰⁾, Gilman⁽⁸⁾, and Cohen⁽⁶⁾. It has been demonstrated that the isocyanide group enters into an addition reaction with the Grignard reagent; it also enters into reactions with sulfur and chlorine at temperatures above 100°C , with the formation of RNCS and $\text{RNC}(\text{Cl})_2$, respectively. Furthermore, it adds acid chlorides to give alkylimido chlorides, $\text{RN}:\text{C}(\text{Cl})\text{COR}$.

Sachs and Loevy⁽²³⁾ give the complete procedure for the preparation of benzaldehyde by a reaction involving phenylmagnesium bromide and methyl isocyanide. No other aldehydes are reported to have been synthesized by this method. On the basis of the results obtained from attempted interaction between phenylmagnesium bromide and various aliphatic and aromatic isocyanides, Gilman and Heckert⁽⁹⁾ concluded that only methyl isocyanide was of sufficient reactivity to combine with the Grignard reagent.

The desirability of developing the method of Sachs and Loevy into a good aldehyde synthesis is apparent, since aldehydes are the starting materials from which a large number of important compounds may be made.

The selection of the organocadmium compound as an alternative organometallic compound was prompted by the conclusions drawn from the experimental work of Gilman and Nelson⁽¹⁰⁾, and de Bonneville⁽³⁾. These workers

found that the relatively lower reactivity of the organocadmium compounds caused the arresting of subsequent harmful interaction between the products formed during an initial stage. Inasmuch as organometallic compounds differ generally in degree or rate of reaction, rather than in kind, it was assumed that the organocadmium compound would add to the isocyanide group in a manner similar to that of the Grignard reagent. It was hoped that a single addition product would result from the reaction between the carbylamine and the organocadmium compound.

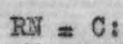
Gilman and Nelson⁽¹⁰⁾ have treated the subject of organometallic compound preparation quite extensively; however, some disagreement exists between these men and Cason⁽⁵⁾ with regard to the stability of organocadmium compounds at elevated temperatures. According to the latter, the organocadmium compounds can be prepared at room temperature without decomposition of the product, while Gilman and Nelson state that a cooled reaction mixture is necessary to prevent decomposition. Cason's procedure was the one used in the preparation of the organocadmium compounds in this work.

n-Butyl isocyanide was selected instead of methyl isocyanide as a suitable carbylamine because of the greater convenience in handling, and also to check Gilman's observation on the unsuitability of the higher molecular weight isocyanides.

Part I includes the synthesis of 2-methyl butanal from a reaction between n-butyl isocyanide and secondary-butylcadmium bromide.

III. THEORETICAL DISCUSSION

A great deal of work has been done in order to ascertain the electronic configuration of the isocyanide group. Two structures are now regarded as most nearly representing the configuration. Nef⁽¹⁹⁾, an early investigator, suggested the structure I which would involve a sextet of electrons on the carbon atom. Langmuir, in 1919, proposed form II. Actual measurements of dipole moments carried out by Hammich, Sedgwick, New and Sutton^{(13), (14)} tend to confirm the validity of form II. Additional support of form II is given by the parachor values obtained by Lindemann and Wiegreb⁽¹⁸⁾.

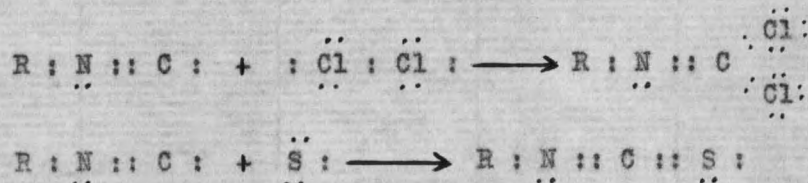


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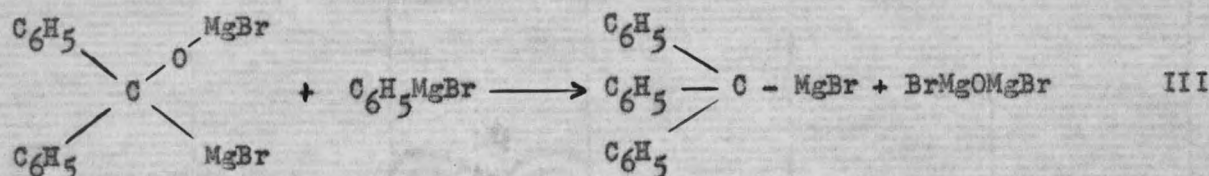
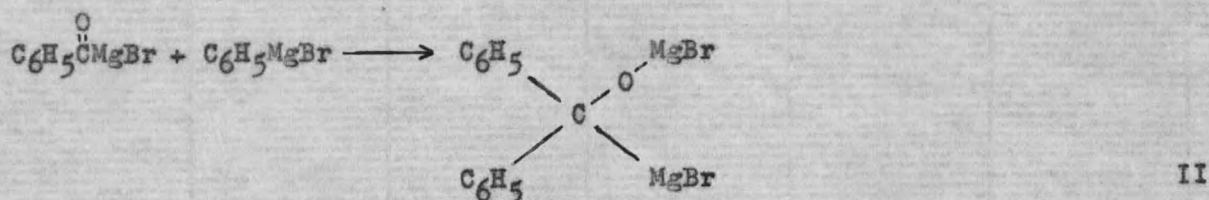
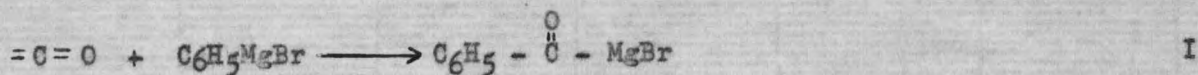
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Structure II is the semipolar form and the stable configuration, while I, the sextet structure, is regarded as the active form. The configurations presented can easily account for such addition products as alkylimino-carbonyl chloride and alkyl isothiocyanate from a reaction between an isocyanide and chlorine and sulfur respectively.



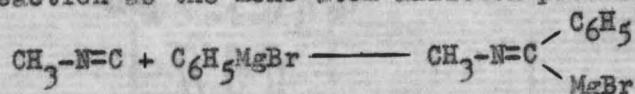
The conclusions drawn from the experimental work of Gilliland and Blanchard⁽⁷⁾ on the reactions between carbon monoxide as nickel carbonyl and phenylmagnesium bromide are presented here so that an analogy may be made between their work and the mechanism of the addition of an organocadmium compound to an isocyanide.

Gilliland and Blanchard postulated that in the reaction between nickel carbonyl and an excess of the Grignard reagent, phenylmagnesium bromide, the reactions shown below took place. They assumed that cleavage of the nickel carbonyl molecule took place simultaneously with the addition of the Grignard reagent; thus, we have:

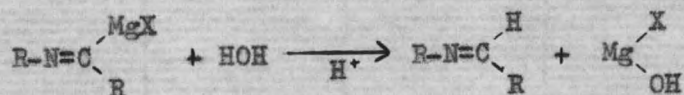


Hydrolysis of the final product yielded an abundance of triphenylmethane, which tends to substantiate the mechanism proposed above. It is to be noted that in step I, the phenylmagnesium bromide added to the carbon atom. This, of course, is contrary to the general mode of addition, according to which $RMgX$ adds as two fragments, R and MgX , to two different atoms.

Additional evidence of the addition of the Grignard reagent to a single atom is furnished from the work of Sachs and Loevy⁽²³⁾. These men obtained benzaldehyde from the hydrolysis of the reaction mixture of methyl isocyanide and phenylmagnesium bromide. They represented the initial step of the foregoing reaction as the mono-atom addition product.



The hydrolysis of the addition product formed from a reaction of the Grignard reagent and a carbonyl containing compound, causes the cleavage of the MgX and its simultaneous replacement by a hydrogen atom. It was, therefore, assumed that a similar reaction would result from the hydrolysis of the addition product between an alkyl isocyanide and an organomagnesium compound with the formation of a Schiff's base.



According to Gilman⁽⁸⁾ the hydrolysis of a Schiff's base occurs with the formation of an aldehyde as one of the products. On this basis, the synthesis of benzaldehyde by the method employed by Sachs and Loevy can logically be explained.

Due to the similarity existing between the mode of reaction of organomagnesium compounds and organocadmium compounds, it was believed that an aldehyde would result from a series of reactions employing organocadmium compounds in place of the organomagnesium compounds.

IV. EXPERIMENTAL

The compounds, both intermediate and final, which were used in this investigation, were prepared according to standard procedures.

Silver cyanide: One hundred and thirty grams (.845 mole) of silver nitrate was reacted with 55 g (.845 mole) potassium cyanide in an aqueous medium, whereupon the insoluble silver cyanide precipitated from the solution.



The precipitated silver cyanide was filtered by suction and washed with several portions of water, and then thoroughly dried in the dark. (If the reaction is carried out in the presence of white light, the product will be gray-black in color instead of white.)

Yields as large as 94-98 percent of the theoretical were obtained from the foregoing reaction. The pure salt has a molecular weight of 133.90 and exists as white hexagonal crystals which decompose at 320°C. It is only slightly soluble in water, but is soluble in potassium cyanide and ammonium hydroxide.

n-Butyl isocyanide: The procedure followed was that given by Calmels⁽⁴⁾: One hundred grams of n-butyl iodide and 150 g of dry silver cyanide were placed in a round bottom flask which was fitted with a reflux condenser, and this reaction mixture was heated to 130°C on an oil bath for one and one-half hours. The operation was then interrupted, as the extraction of the isocyanide is easier if the contents of the flask do not become too dark in color. Water and potassium cyanide were added to the double salt, $\text{C}_4\text{H}_9\text{NC}, \text{AgCN}$, whereupon an oily layer of n-butyl isocyanide appeared. It

was found from experience that approximately one mole of potassium cyanide should be added to the reaction mixture for each .5 mole of the isocyanide expected based on the theoretical yield.

The contents of the flask were then steam distilled, and there appeared two layers in the receiving flask; the upper layer consisted of n-butyl isocyanide and the lower one of water. These layers were separated by the use of a separatory funnel, and the n-butyl isocyanide was dried over sodium hydroxide pellets.

The isocyanide was allowed to remain in contact with the drying agent until several hours before use. It was then distilled, and that fraction which boiled between 113° - 122°C was collected and used in the experiment.

A variance in the yields was caused by the presence of water in the silver cyanide. As a general rule, the best yields were obtained from a thoroughly anhydrous salt which had been dried at 120°C from 10 to 20 hours. The average yield was about 26 g (.313 mole) or about 58 percent of the theoretical.

Secondary-butylmagnesium bromide: The procedure for the preparation of the Grignard reagent is given by Gilman, Zoellner and Dickey⁽¹¹⁾, and in the present case consists of a reaction between secondary-butyl bromide and magnesium turnings in absolute ether. In a three-necked flask fitted with a reflux condenser, mercury seal stirrer, and a drop funnel were placed 6 g (.25 mole) of dry magnesium turnings, 25 cc absolute ether, 15-20 drops of secondary-butyl bromide, and a small crystal of iodine. The latter tends to activate the surface of the magnesium, thus promoting a better reaction.

Once the reaction had begun, as indicated by the formation of small bubbles and a slight reflux action, the motor driven stirrer was started. A solution of 34 g (.25 mole) of secondary-butyl bromide and 125 cc of absolute ether was then placed in the drop funnel and allowed to flow into the flask at the rate of one drop per second. The stirring was continued for an additional one-half hour after the contents of the drop funnel had been added to the flask.

During the course of this reaction the apparatus was kept free from moisture by providing the drop funnel and reflux condenser with calcium chloride drying tubes. The reaction mixture was kept in an anhydrous condition as moisture readily causes decomposition of all organometallic compounds.

Secondary-Butylcadmium Bromide: The organocadmium compound was derived directly from the organomagnesium compound, according to the procedure suggested by Cason⁽⁵⁾.

An additional 100 cc of absolute ether was added to the Grignard reagent to keep the organocadmium compound in a more liquid state after its formation. Next, the drop funnel was removed from the three necked flask, and was quickly replaced by a tube which contained 45.8 g (.25 mole) of anhydrous cadmium chloride. The cadmium chloride was added to the secondary-butylmagnesium bromide-ether solution during a period of fifteen minutes, while vigorous stirring of the reaction mixture was effected with the mercury seal stirrer.

Reflux occurred during the addition of the cadmium chloride and for a subsequent one-half hour.

Synthesis of 2 methyl butanal: Twenty and seven tenths grams (.25 mole) of n-butyl isocyanide was added to approximately .25 mole of secondary-butylcadmium bromide prepared according to the above procedure. This addition was carried out at room temperature with constant stirring of the reaction mixture. The mixing of these compounds precipitated a mild reflux action within the containing vessel. Vigorous stirring was continued for a period of four hours after the complete mixing of the reactants. The reaction mixture was then allowed to stand for twenty-four hours.

A light yellow liquid appeared on the surface of the contents of the flask, while the remainder of the solution possessed the characteristic color of the organocadmium compound. An ice-water mixture was then placed around the lower portion of the flask containing the reactants, the stirrer was started, and sufficient time was allowed for the contents of the flask to come into equilibrium with the temperature of the ice-water bath.

During this time, 120 ml of a 6 N sulfuric acid solution was prepared, and this, too, was cooled to the temperature of an ice-water mixture. The hydrolysis of the reaction mixture was then accomplished by adding the cold dilute acid dropwise. During the time of hydrolysis, the reaction had to be watched carefully, and a temperature of approximately 0°C was maintained within the reaction vessel. The most critical part of the hydrolysis came during the addition of the first few cc of the dilute acid.

When the hydrolysis was complete the ice-water bath was removed, the stirring stopped, and within several minutes three layers formed in the flask. The bottom layer was mainly water, while the top layer was largely ether; the middle layer was separated by use of a separatory funnel and

transferred to a 200 ml round bottom flask.

This liquid, dark red in color, was then steam distilled, and the distillate, consisting of two layers, was collected in a 125 ml Florence flask. These layers were separated with the aid of a separatory funnel. The upper layer contained ether, and what later proved to be an aldehyde, while the bottom layer was the aqueous portion. This aqueous layer was extracted with several small portions of absolute ether, and the extracts were combined with the upper layer of the steam distillate. The ether portion was then dried, first by anhydrous sodium sulfate, and later by "Drierite" (calcium sulfate).

The ether solution was dried for 24 hours, then transferred to a 50 ml round bottom flask which was fitted with a small fractionating column, and the ether was removed. There remained approximately 1.5 ml of a light yellow liquid which was distilled with a small test tube distilling apparatus. The boiling point was 86-87°C at 640 mm. The product had a strong characteristic odor of aldehyde. Small portions were tested as indicated below.

Tests of Confirmation:

The information listed below was obtained from Huntress and Mullikin⁽¹⁵⁾ regarding 2 methyl butenal.

B. P. 92-93°C

D_4^{20} 0.80294

n_D^{20} 1.38960

2,4 dinitrophenylhydrazone: M. P. 120.5°C

Two qualitative tests were first conducted in order to detect the presence of an aldehyde; these were accomplished with the use of Tollen's reagent and Schiff's reagent. The preparation of these classification reagents, and the procedure for their use is given by Shriner and Fuson (28).

Three drops of the distillate obtained as product from the above procedure were added to approximately 3 cc of the freshly prepared Tollen's reagent. A positive aldehyde test began to appear within 30 seconds after mixing the liquids, and consisted of a coating of free silver deposited on the walls of the containing vessel.

The Schiff's test was carried out in a similar manner by the addition of several drops of the unknown liquid to 3 cc of the fuchsin-aldehyde reagent. Within a few seconds the colorless fuchsin aldehyde reagent turned pink, which indicated the presence of an aldehyde group in the unknown liquid.

The index of refraction of the product was found to be 1.392. The value listed by Mullikin for an authentic sample of 2-methyl butanal is $n_D^{20} = 1.38960$.

The boiling point as previously indicated was 86°-87°C at 640 mm. The corrected value of 91.6° at 760 mm was obtained through the use of the following equation.

$$\text{B. P. (corrected)} = \text{B. P. (observed)} + \left[\frac{273 + \text{B. P. (obs)}}{f} \times \frac{760 - \text{atmos. pres.}}{10} \right]$$

where f has the constant value of 850 for non-associated liquids.

Close agreement existed between the confirmatory tests and the data pertaining to 2-methyl butanal; therefore, it was decided to confirm the identity of the unknown liquid by means of derivatization.

Preparation of the Derivative

The procedure followed in the preparation of the derivative is that given by Allen⁽¹⁾. The 2,4-dinitrophenylhydrazine reagent was prepared by dissolving 2 g of 2,4-dinitrophenylhydrazine in 15 cc of concentrated sulfuric acid. This solution was then added, with stirring, to 150 cc of 95 percent alcohol. The solution was diluted to 500 cc with distilled water, mixed thoroughly and filtered.

To 5 cc of the 2,4-dinitrophenylhydrazine solution contained in an eight inch test tube were added 5 drops of the unknown sample and 5 cc of 95 percent alcohol. This mixture was heated to boiling over a low flame, and two drops of concentrated hydrochloric acid were added. The heating was continued for an additional two minutes, and the solution was allowed to cool. Next, distilled water was added drop by drop to incipient cloudiness, and upon further cooling under a cold water tap, the derivative began to crystallize out. The precipitate was collected by centrifugation, dissolved in alcohol and re-precipitated by the addition of water.

The final product consisted of several milligrams of a light yellow crystalline solid, which was allowed to air dry for several days.

The melting point of this material was 119-120°C. The melting point of the 2,4-dinitrophenylhydrazone derivative of 2-methyl butanal is given as 120.5°C.

Assuming complete reaction in the preparation of secondary-butylmagnesium bromide and secondary-butylcadmium bromide, the theoretical yield from the reaction between n-butyl isocyanide and secondary-butyl-

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cadmium bromide is 22.3 g. The actual yield was found to be 1.2 g or 5.4 percent of the theoretical.

V. DISCUSSION OF EXPERIMENTAL RESULTS

Although a larger percent of the theoretical yield is to be desired, the results indicate that the process as outlined is a successful method for the preparation of 2-methyl butanal from n-butyl isocyanide and secondary-butylcadmium bromide.

The mechanism of the reaction presented in the abstract appears to be a logical explanation of the process, although no tests were conducted to establish the exact mechanism of the reaction. The reactions presented can account for the formation of the aldehyde, and were formulated before any of the experimental work was undertaken.

This process as outlined does not appear to be applicable to large scale application either industrially or in the laboratory. This fact is based upon the low yield of aldehyde obtained, the necessity of preparing a fresh organocadmium compound before each run, the high cost of preparation of the isocyanide if prepared by the method indicated, and the extreme unpleasantness of working near and handling the isocyanides due to their repulsive odor and toxicity.

Results of a more significant nature may be realized by employing different combinations of reactants. Methyl isocyanide would perhaps be a more suitable carbylemine, as it appears to be more reactive than the other members of its homologous series. Further, the wide variety of organometallic compounds makes available an almost limitless number of starting materials.

The participation of n-butyl isocyanide in this type of reaction may be assumed to be contrary to the findings of Gilman, who, however, based

his report on the reactions between carbylamines and organomagnesium compounds.

VI. SUMMARY

1. A reaction has been shown to occur between secondary-butylcadmium bromide and n-butyl isocyanide.
2. The hydrolysis of this reaction mixture yielded 2-methyl butanal in the amount of 5.4 percent of the theoretical. Production of an aldehyde through the use of n-butyl isocyanide appears to be contrary to the results obtained by previous investigators.
3. The nature of the aldehyde obtained as product is determined by the alkyl halide employed in the organocadmium compound preparation, and is not dependent upon the isocyanide used.
4. A logical mechanism is suggested which outlines the course of the reaction.
5. It is suggested that subsequent investigation using different organo-metallic compounds and other isocyanides, could prove significant from the standpoint of ascertaining which reactants produce the greatest yield of aldehyde.

Part II.

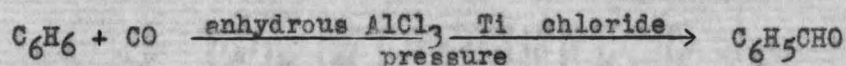
I. ABSTRACT

A reaction mixture consisting of the sodium salt of nitroethane and nickel carbonyl in a solvent of cyclohexane, was subjected to high pressures of carbon monoxide. This reaction mixture yielded, upon hydrolysis, a substance possessing a solubility which could not readily be accounted for. This substance is not obtained in the absence of nickel carbonyl, or when cyclohexane itself is subjected to carbon monoxide under pressure in the presence of nickel carbonyl. The unidentified substance is decomposed by steam distillation, simple distillation, and vacuum distillation, and cannot be crystallized satisfactorily even at low temperatures. Positive Schiff's and Tollen's tests were obtained by use of the appropriate reagent and the unknown substance. Derivatization of the unidentified material has not been possible.

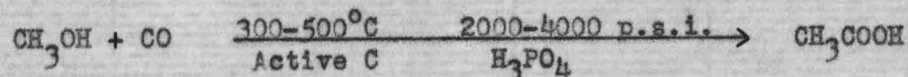
Additional investigation of the unidentified substance is being conducted.

II. INTRODUCTION

The use of carbon monoxide as a source of the carbonyl group in addition reactions is of great importance, and consequently, has found many applications of commercial and technical value. According to Guthke⁽¹²⁾, the synthesis of benzaldehyde may be accomplished according to the following reaction:



The synthesis of aldehydes by reactions between olefins, carbon monoxide and hydrogen in the presence of cobalt carbonyl under conditions of high pressure has also been demonstrated^{(25) (32)}. This synthesis is known as the "oxo" process. Furthermore, considerable investigation has been conducted regarding the reactions between carbon monoxide at high pressures and esters, ethers, and alcohols⁽³³⁾. The production of acetic acid in good yield has been reported by Singh and Krase⁽²⁹⁾ according to the following equation:

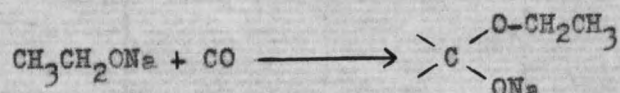


The adaptability to industry of high pressure methods of synthesis has greatly intensified the amount of investigation in this field within recent years. The numerous literature references pertaining to high pressure reactions was one factor which prompted the investigation considered in this paper. The original aim was the synthesis of 2-nitropropanal by a reaction between the sodium salt of nitroethane and carbon monoxide under conditions of high pressure.

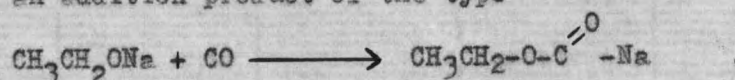
III. THEORETICAL DISCUSSION

Up to the present time no work has been reported which deals with a reaction involving carbon monoxide and the salts of nitro paraffins; in fact, it appears that very little investigation has been conducted using carbon monoxide and organic salts of any type.

Scheibler and Frikell⁽²⁶⁾ report the formation of a bi-valent carbon atom resulting from the high pressure reaction between carbon monoxide and sodium ethylate.



The findings of these workers, however, have never been substantiated, and according to Stehler⁽³⁰⁾, the above reaction is incorrect and Stehler suggests, instead, an addition product of the type



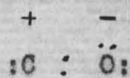
The existence of an addition product between the salt and carbon monoxide does seem to have been substantiated even though conclusive proof as to the correct mechanism appears to be lacking.

The conclusions drawn from the work of Hamnisch, et al⁽¹³⁾, based upon results obtained from parachor and dipole moment measurements, establishes the structure of carbon monoxide as being:



The work of Pauling and Sherman⁽²²⁾, however, indicates that resonance exists between several structures. Their conclusions were based upon evidence gathered from resonance energy data and electric dipole moment

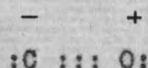
measurements. It now appears logical to assume that the carbon monoxide molecule resonates about equally among the three structures



I

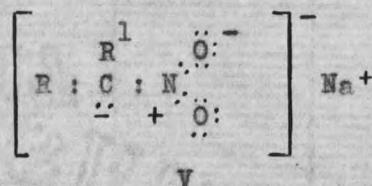
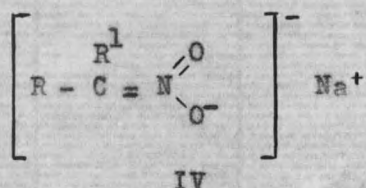


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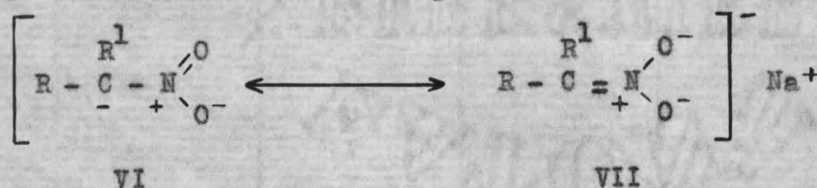


III

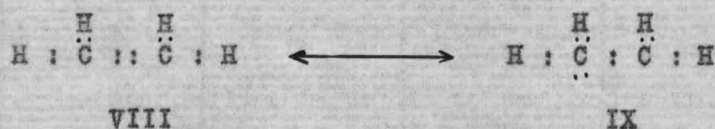
A similar situation was found to exist regarding the structure of the sodium salts of nitro paraffins. Some original work pertinent to the salt formation of nitro paraffins was done by Kuhn and Albrecht⁽¹⁷⁾ and these workers concluded that the salts are correctly represented by the structures



Upon further investigation Kornblum⁽¹⁶⁾ and his associates determined experimentally that resonance actually exists within the salts of nitro paraffins, and that a slight modification of the above structure was necessary. The resonance structure presented is

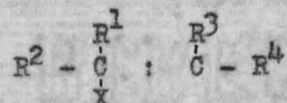


Whitmore⁽³⁴⁾ suggests that ethylene, and olefins in general, may be converted into "activated substances" under suitable conditions. The proposed electronic configuration for ethylene in the "normal" and "activated" forms are:

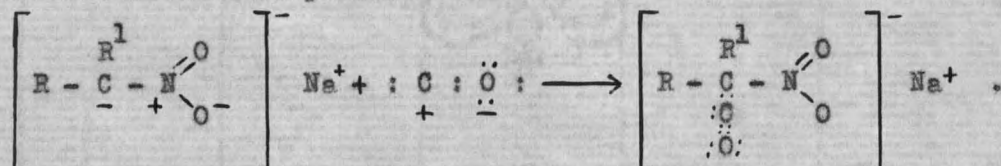


Form VIII, the normal form, is seen to contain a double bond, whereas in form IX, the activated molecule, the double bond is opened and a pair of electrons has become associated with the carbon atom on the left.

The validity of form IX has been reasonably well substantiated by the work of Bartlett and Tarbell⁽²⁾, and, Terry and Eichelberger⁽³¹⁾. Bartlett and Tarbell have shown that the first step in the addition of halogens to ethylene linkages leads to the formation of an ion of the type



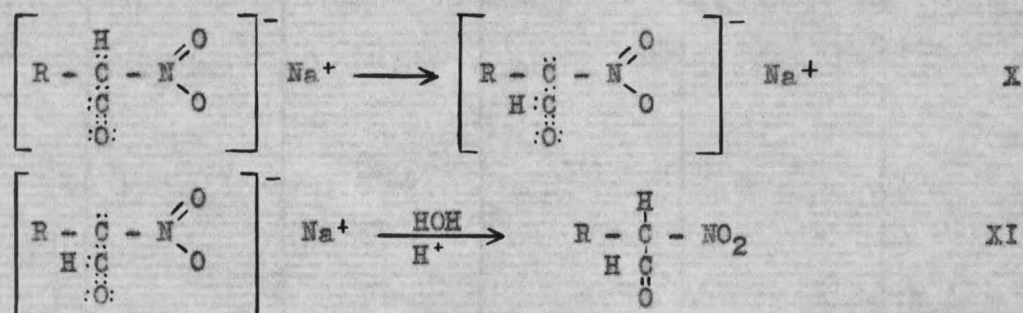
The similarity existing between the activated form of ethylene and that of form VI of the sodium salt of a nitro paraffin is at once apparent. The mechanism proposed for the addition of carbon monoxide to form VI of the sodium salt of a nitro paraffin is



An equivalent addition product is also assumed to result from a reaction between form VII of the nitro paraffin salt and carbon monoxide.

In the investigation under consideration nickel carbonyl was employed as a catalyst, thus drawing a closer analogy between the carbon monoxide-nitro paraffin salt reaction, and that of the "oxo" process for the preparation of aldehydes from a reaction involving olefins, carbon monoxide, and hydrogen in the presence of cobalt carbonyl. Furthermore, the use of

nickel as a catalyst has been reported by Schalch⁽²⁵⁾ in a process involving a reaction between olefins and carbon monoxide for the preparation of oxygen containing derivatives. Although the "oxo" process employs hydrogen as a necessary component of the reaction mixture, it was assumed that hydrolysis of the sodium salt of nitroethane-carbon monoxide reaction mixture would result in aldehyde formation according to the following mechanism:



The hydrogen ion migration shown in X is a logical step in the formation of a more stable molecule, and would very likely occur.

The product resulting from the above reaction is 2-nitropropanal. Theoretically, a compound of this type should enter into a great many reactions, making possible the synthesis of a wide variety of new materials. By employing the right conditions, reduction of 2-nitropropanal should yield a mixture of 2-nitropropanol, 2-aminopropanal, and 2-aminopropanol. The oxidation of 2-nitropropanal should yield alpha-nitro-propionic acid. Acetal formation should be possible from a reaction between 2-nitropropanal and an alcohol. Thus it is apparent that 2-nitropropanal could form the starting material from which a large number of compounds could be prepared.

IV. EXPERIMENTAL

The starting materials were the sodium salt of nitroethane, cyclohexane, carbon monoxide and nickel carbonyl. The latter three compounds were purchased from an industrial source and employed without further purification.

Apparatus:

A complete description of the American Instrument Company's high pressure reaction apparatus is not presented here for the equipment is of a standard type. Essentially, the apparatus consists of a heavy alloy steel bomb having a capacity of 125 cc which holds the reacting materials, and which is fitted with a pressure gage which indicates the internal pressure of the bomb in pounds per square inch. The bomb-pressure gage unit is mounted in a heating jacket, and the entire assembly is agitated by means of motor-rockerarm system. The heating of the bomb is automatically effected by means of an electric pyrometer used in conjunction with a thermocouple which is inserted through the end of the heating jacket into the rear portion of the bomb. The compressed gas, as obtained from the metal cylinders, is subjected to further compression by the use of a manually operated oil booster pump; the charge of compressed gas is then delivered from the booster pump into the bomb through a series of four connections. Pressures of approximately 8000 pounds per square inch (534 atmospheres) can safely be maintained within the bomb. A pressure in excess of 8000 p. s. i. causes the rupture of the safety disc, which automatically releases the entire bomb charge. Temperatures up to 400°C can be obtained within the reaction mixture.

Preparation of the Sodium Salt of Nitroethane

This substance was prepared in a manner similar to that suggested by Kuhn and Albrecht⁽¹⁷⁾. Three hundred and twenty cc (7.95 mole) of methanol was placed in a three neck flask which was provided with a motor driven stirrer, reflux condenser, and a cork. The flask was surrounded by an ice-water bath, as the maintenance of a low temperature throughout the reaction was necessary. Twenty three grams (1 mole) of sodium wire was added to the cold methanol in approximately five portions over a period of ten minutes. Vigorous stirring was effected during the addition of the sodium, and complete disappearance of the sodium was accomplished within five minutes after the last portion had been added.

The contents of the flask were then transferred to a large beaker, whereupon 75 cc (1 mole) of nitroethane was added with stirring. Almost immediately, the insoluble sodium salt of nitroethane precipitated out, and was removed from the excess methanol by suction filtration.

The filtered salt was washed with several portions of cold methanol, placed in a large crystallizing dish, and then allowed to air dry. (Under no circumstances should the salt be dried in an oven, as it appears to be extremely explosive while still moist with methanol. This information was obtained at the expense of an electric drying oven which was completely demolished as a result of such an explosion.)

The sodium salt of nitroethane was obtained in yields of approximately eighty-five percent of the theoretical according to the procedure just described.

Typical Procedure for Experimental Runs

The procedure of charging the bomb and the subsequent hydrolysis of the reaction mixture used during the course of this investigation is outlined as follows: Ten grams (.103 mole) of the dry sodium salt of nitroethane was mixed with 35 ml (.324 mole) cyclohexane and one half ml (.00385 mole) of nickel carbonyl. The mixture was placed in the bomb and its consistency was sufficiently liquid to allow thorough mixing during the time the bomb was being agitated. Carbon monoxide was then forced into the reaction mixture at pressures ranging from 2400 p. s. i. to 5000 p. s. i. Temperatures of from 23°C to 175°C were maintained during the course of the reaction.

After sufficient time had been allowed for the reaction, usually about 30 minutes, the bomb was removed from the heating jacket, cooled in a water bath if necessary, and vented in a hood. The pressure gage and bomb head were then removed and the contents of the bomb were transferred to a three neck flask. The hydrolysis which followed was carried out in a hood also, for the presence of nickel carbonyl was evident from its characteristic odor. The three neck flask was provided with a reflux condenser, motor driven stirrer, and a drop funnel. In the drop funnel were placed a cold solution of 15 cc distilled water and 2.75 cc (.0525 mole) concentrated sulfuric acid (sp. gr. 1.8351); this was allowed to flow dropwise into the contents of the flask. Very little heat was generated during the course of the hydrolysis, and after the contents of the drop funnel had been added to the flask, stirring was continued for an additional five minutes.

This reaction mixture was then transferred to a separatory funnel whereupon three immiscible layers-A, B, and C formed. Layer A, the top layer, was found to consist largely of cyclohexane; a small amount of the regenerated nitroethane was also contained in this layer as indicated by the boiling points obtained by fractionation. Layer B, the material with which this work is primarily concerned, was present in the amount of approximately 4 cc. The bottom layer C, proved to be the aqueous layer which contained some dissolved inorganic salts.

Layer B was customarily dried with sodium sulfate, followed by small quantities of calcium sulfate. Layer B gave off a gas similar in character to that ensuing from a carbonated beverage. Small bubbles of gas escaped from its surface at a very high rate, and a 4 cc portion would exhibit this phenomenon for a period of several days with decreasing gas emission. It was found that this bubbling activity could be halted by solidifying the unknown liquid in a mixture of dry ice and acetone. Bubbling would resume once the frozen substance was permitted to liquify. Layer B was found to be insoluble in cyclohexane, but soluble in nitroethane, ether, alcohol and various other organic solvents. Layer B, obtained from runs in which the bomb temperature was about 150°C, appeared to polymerize spontaneously after standing for a period of three or four days, giving a dark colored, viscous, insoluble material.

Varying conditions of pressure, temperature, catalyst and length of time permitted for reaction were employed in an attempt to obtain additional information regarding the formation of the three immiscible layers upon hydrolysis of the reaction mixture.

A. Effect of Variations in Procedure on Yield of Product

1. Heat

It was found that the application of heat to a typical bomb charge, had little or no effect upon the yield of layer B. Temperatures of from 150° to 185°C were maintained for periods of from one to six hours, accompanied by various pressures of carbon monoxide. The hydrolysis product of a heated reaction mixture appeared to be identical to that of an unheated mixture, except that its color was somewhat darker.

2. Omission of Nickel Carbonyl

Several attempts were made to determine the source of layer B; the procedure employed is essentially the one described below. Ten grams of the dry sodium salt of nitroethane in a solvent of 35 cc of cyclohexane was subjected to a pressure of 3115 p. s. i. of carbon monoxide for a period of 30 minutes. No heat was applied to the reaction mixture. Upon the subsequent hydrolysis of the bomb charge only two layers appeared, the usual middle, red-black layer, being completely absent.

3. Omission of Salt

When the bomb charge consisted of one half cc of nickel carbonyl and 35 cc of cyclohexane under a pressure of 3115 p. s. i. of carbon monoxide, the hydrolysis product consisted of only two layers, layer B again being absent. It was then concluded that both nickel carbonyl and the sodium salt of nitroethane were necessary bomb charge components for the formation of the three layers upon hydrolysis.

4. Use of Salt Containing Methyl Alcohol

Several runs were made using the standard bomb charge; however, in these instances the sodium salt of nitroethane was not completely free from methanol. On one occasion the initial pressure of 2500 p. s. i. of carbon monoxide at 25°C increased to a value of about 3600 p. s. i. at a temperature of 150°C. Shortly after this pressure had been attained, the safety disc was ruptured, indicating that a tremendous pressure had suddenly been developed within the bomb. There remained only a small char residue of the reactants within the bomb. In the case of the other runs under consideration, those employing a salt moist with methanol, either no middle layer or a middle layer with a greatly reduced percent of yield resulted from the hydrolysis of the bomb charge.

5. In Presence of Hydrogen

On one occasion a typical bomb charge under a pressure of 2000 p. s. i. of carbon monoxide was subjected to an additional 1600 p. s. i. of hydrogen, and a temperature of 150°C was employed. An extremely high pressure of 7600 p. s. i. was developed within the bomb during the course of the heating; however, the final hydrolysis product contained the customary three immiscible liquids which appeared to be identical with those obtained when the hydrogen had been omitted.

6. Hydrolysis of Run Previous to Pressuring with Carbon Monoxide

A typical bomb charge was hydrolyzed without first being subject to carbon monoxide under high pressure. The hydrolysis caused the formation of only layers A and C. Layer B was non-existent. The heavier layer consisted of water which contained some soluble inorganic material, probably

sodium sulfate. The top layer was fractionated and was found to consist of two fractions; these were identified by means of their boiling points, and proved to be nitroethane and cyclohexane.

7. Variations in Pressure

It was observed that a pressure drop of approximately 175 p. s. i. resulted when the reactants in the bomb were nickel carbonyl, cyclohexane, and carbon monoxide, the salt being omitted. A series of runs was made by increasing the carbon monoxide pressure from 2400 p. s. i. to 4480 p. s. i. at intervals of about 500 p. s. i. In every case the total pressure drop over a period of 30 minutes was found to be approximately constant at about 175 p. s. i. In the cases of greater initial pressure, it was noticed that the pressure drop of 175 p. s. i. was obtained within five to ten minutes, there being no noticeable pressure change after that time. The same total pressure drop was found to result when a standard bomb charge was employed. The theoretical pressure drop resulting from the addition of one mole of carbon monoxide to one mole of the sodium salt of nitroethane at a pressure of 3000 p. s. i. and a temperature of 25°C is 5700 p. s. i. In the case of a typical bomb charge the theoretical pressure drop is 570 p. s. i.

A total pressure drop of 175 p. s. i. indicated a pressure drop of approximately 31 percent of the theoretical.

B. Attempts at Purification of Layer B

1. Distillation at Ordinary Pressure

The first attempt made to isolate and purify layer B was by the method of ordinary distillation. A small distilling flask-water cooled condenser

outfit was employed. Normal distillation took place during the initial stages of heating, and a boiling point of $75^{\circ}\text{--}85^{\circ}\text{C}$ was recorded. Suddenly, with the distillation about one-quarter complete, the temperature within the distilling flask rose to 135°C , and there remained only a charred residue of layer B.

2. Vacuum Distillation

Vacuum distillation was employed next in an attempt to obtain layer B in a pure state. In the first instance, a vacuum of 40 mm was maintained, and an oil bath held constant at a temperature of 45°C was used to remove any low boiling material that might have been present as impurities within layer B. A few cc of distillate was obtained at this temperature, but as the temperature of the oil bath was raised, decomposition of the material within the flask took place. On several occasions the decomposition was so violent that some damage was caused to the vacuum distillation apparatus. Vacuum distillation under pressures as low as 10 mm was tried, but in every case complete charring of layer B resulted. Nitroethane can be distilled in a normal manner without danger of spontaneous decomposition.

3. Steam Distillation

The distillate resulting from the steam distillation of layer B consisted of two immiscible liquids. These liquids were identified by means of their boiling points and were found to be water and nitroethane. Although layer B was insoluble in cyclohexane before being subjected to steam distillation, the nitroethane portion of the distillate was readily soluble in cyclohexane.

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4. Crystallization at Low Temperature

An attempt was made to crystallize layer B at a low temperature, remove the solvent, and thus retain a pure product. Approximately one cc of layer B was dissolved in three cc of ethanol contained in a test tube; this vessel was placed in an acetone-dry ice mixture which maintained a temperature of about -83°C . Within a period of several minutes, crystals formed in the ethanol solution. It is to be noted that the melting point of pure ethanol is known to be -112°C . A small Hirsch filter funnel, surrounded by an acetone-dry ice mixture, was used to aid in the separation of the crystals from the solvent. Effective separation of the crystals by this method was not practical, although a few individual crystals were isolated. The isolated substance was found to be largely inorganic in nature.

C. Attempts to Identify Layer B and Prepare Derivatives

(1) Schiff's and Tollen's Test

Schiff's and Tollen's tests were conducted in an attempt to determine the presence of an aldehyde linkage within layer B. Conclusive tests were not obtained, however, for it was found that nitroethane also caused the appearance of a positive test in both cases.

It was observed that when equal amounts of layer B and nitroethane were added to the above-mentioned reagents contained in different test tubes, positive tests were developed much more quickly in the case of layer B.

(2) 2,4-dinitrophenylhydrazine and Semicarbazide Hydrochloride

It was impossible to obtain a reaction between this liquid and 2,4-di-

nitrophenylhydrazine or semicarbazide hydrochloride. The method for the preparation of these derivatives is that described by Shriner and Fuson⁽²⁸⁾.

(3) Schiff's Base Formation

An attempt was made to form a Schiff's base by interaction of layer B and p-toluidine. There appeared to be no reaction.

(4) Acetal Formation

A standard reaction for acetal preparation involves interaction between an aldehyde and an alcohol. In the present case layer B was heated with an equivalent amount of alcohol in the presence of calcium chloride. The reaction mixture contained no acetal, thus the identity of layer B was still unknown.

(5) Oxidation

It was observed that a one percent solution of potassium permanganate was readily reduced when brought into contact with layer B; it was, therefore, postulated that an oxidizable group existed in the unidentified substance. Nitroethane was found to exhibit this property also.

The oxidation was carried out using a five percent potassium permanganate solution. This was added to the typical bomb charge after a pressure of 4200 p. s. i. of carbon monoxide had been exerted on it for a period of 30 minutes but before hydrolysis was attempted. The excess potassium permanganate and precipitated manganese dioxide were separated from the aqueous solution by centrifugation. The water portion was distilled in vacuo to a volume of about 15 cc. By the addition of absolute alcohol to the aqueous layer and by repeated vacuum distillations, this water was re-

moved as a component of the azeotropic alcohol-water mixture. There remained in the alcohol solution a gray-white solid which was separated from the ethanol by filtration. The solid was then air dried.

The hydrolysis of this salt with the calculated amount of sulfuric acid was carried out in a small three neck flask in a solution of absolute ether. A brown gas, probably nitrogen dioxide, was given off during the hydrolysis. The ether layer was dried with phosphoric anhydride and subsequently vacuum distilled. There remained in the distilling flask a yellow-white solid which was recrystallized from carbon disulfide. The pure crystals melted at a temperature of 80°C . A neutralization equivalent was run using .1235 g of the recrystallized solid dissolved in 50 cc of alcohol; the solution was titrated with standard sodium hydroxide (.1685 N) using phenolphthalein as an indicator. Seven and eleven one hundredths cc of alkali was required for neutralization.

$$\text{N. E.} = \frac{\text{weight of sample} \times 1000}{\text{volume of alkali} \times \text{normality}}.$$

The molecular weight is equal to the product of the neutralization equivalent and the number of acidic groups in the molecule. The molecular weight was calculated as 103 on the assumption that the unknown solid contained one carboxyl group. Nitro-acetic acid has a melting point of 84° , and a molecular weight of 105; thus it was concluded that nitro-acetic acid, and not alpha-nitropropionic acid, was the product obtained from the oxidation of the bomb charge.

(6) Reduction

The reduction of layer B was attempted at hydrogen pressures ranging from 50 p. s. i. to 3000 p. s. i. Absolute ethanol was used as a solvent. Two catalysts were used, one being U. O. P. nickel catalyst, and the other Adam's platinum dioxide. In every case the reduction products smelled strongly of amine, probably due to the presence of ethylamine; furthermore, the entire reduced liquid distilled at a temperature below 110°C . All of the products which might result from the reduction of 2-nitropropenal, would either be solid at room temperature, or have a boiling point within the range $165^{\circ}\text{--}195^{\circ}\text{C}$. Reduction was also attempted using hydroiodic acid and red phosphorus according to the procedure suggested by Scarrow and Allen⁽²⁴⁾. The results were negative.

D. A Reaction Involving the Salt of 2-Nitropropene

During the course of this work it appeared that a salt of a nitro compound which contained no alpha hydrogen might yield a final product of a more stable nature. The sodium salt of 2-nitropropene was employed in attempt to confirm this theory.

On several occasions the sodium salt of 2-nitropropene was mixed with cyclohexane and nickel carbonyl, and placed under a high pressure of carbon monoxide. Hydrolysis caused the formation of a light green solid, which was easily sublimed to a pure white solid. The melting point of this substance was found to be $76^{\circ}\text{--}77^{\circ}\text{C}$. The sublimed solid dissolved in colorless organic solvents with the production of a green-blue colored liquid; this is characteristic of nitroso and pseudonitroso compounds. Additional

investigation indicated that the white crystalline solid was propyl pseudonitrol, $\text{CH}_3\text{C}(\text{NO}_2)\text{NOCH}_3$. The melting point given by Scholl⁽²⁷⁾ for this compound is 76° .

It was subsequently discovered that the acidification of the sodium salt of 2-nitropropane resulted in the formation of propyl pseudonitrole, thus the carbon monoxide played no part in the reaction. It was further found that propyl pseudonitrole is prepared industrially by a reaction of 2-nitropropane with concentrated alkali⁽²¹⁾. Further investigation using 2-nitropropane was consequently halted.

V. DISCUSSION OF EXPERIMENTAL RESULTS

Steam distillation of layer B yielded nitroethane as one of the products. The fact that nitroethane is soluble in cyclohexane whereas layer B is not, affords proof that a substance different from the starting materials resulted from a typical run.

The experimental results indicate that the hydrolysis product of a typical bomb charge which had not been subjected to high pressures of carbon monoxide contained no layer B, whereas, a pressurized reaction mixture yielded layer B upon hydrolysis. Furthermore, it was experimentally shown that both nickel carbonyl and the sodium salt of nitroethane were necessary reactants for the formation of layer B.

The identical pressure drops resulting from the carbon monoxide pressurizing of a typical bomb charge, and a reaction mixture which contained no salt, suggest that the pressure drop was due to the solubility of carbon monoxide in the solvent.

The instability of layer B, especially at elevated temperatures, may be interpreted as indicating the existence of an extremely unstable molecule. Such a molecule could possibly result from a coordination product formed between carbon monoxide and nitroethane after the hydrolysis of a typical bomb charge. $\text{CO}[\text{CH}(\text{CH}_3)=\text{NO}_2\text{H}]_2$ is suggested as a possible coordination product. This theory can also account for the effervescent activity of layer B.

Carbon monoxide, if released from layer B, could act as a reducing agent, and thus bring about a more quickly developed Tollen's and Schiff's

test, than those resulting from the use of nitroethane and the respective reagent.

The fact that layer B obtained from runs in which the bomb was heated tends to polymerize on standing, suggests the presence of an unsaturated grouping, such as the carbonyl group. An aldehyde group, if present in layer B, should have exhibited the characteristic properties of this group, yet the inability of layer B to enter into reaction with 2,4-dinitrophenylhydrazine, semicarbazide hydrochloride, ethanol, and p-toluidine indicates that 2-nitropropanal was not a constituent of layer B.

Additional investigation of layer B may reveal the true identity of this substance. At present, evidence indicates that carbon monoxide does not react with the sodium salt of nitroethane with the production of a carbonyl group containing compound.

VI. SUMMARY

1. The acid hydrolysis of a pressurized bomb charge consisting of carbon monoxide, nickel carbonyl, the sodium salt of nitroethane in cyclohexane, caused the formation of three immiscible liquids. Liquid A, the top layer, consisted of cyclohexane and nitroethane. Layer B, the middle layer, was the unidentified material. Layer C, the bottom layer, was composed of water and inorganic salts.
2. Layer B was of an unstable nature, and its purification was not possible.
3. The failure of layer B to react with 2,4-dinitrophenylhydrazine, semicarbazide hydrochloride, alcohol and p-toluidine, indicates that 2-nitropropanal was not present.
4. It is suggested that layer B consisted of a coordination compound formed between carbon monoxide and nitroethane.

VII. ACKNOWLEDGMENT

The author wishes to take this opportunity to express his sincere appreciation and thanks to Dr. Laurence O. Binder, Jr. for his personal guidance and inspiration during this research, and to the staff of the Chemistry Department for their many helpful suggestions. He also wishes to thank the Office of Naval Research of the Department of Navy for the grant which made this investigation possible.

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Bruce, John M., Jr.

1. The synthesis of 2-methyl butanol

2. Carbon monoxide and the sodium
salt of nitroethane.

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