MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES
3 4456 0360242 0

[redacted]

ORNL 40 3A
CHEMISTRY-SEPARATIONS
PROCESSES FOR URANIUM

CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION

DECLASSIFIED
CLASSIFICATION CHANGED TO:
BY AUTHORITY OF: TID-1111
BY: N. Johnstone 10-19-56

LABORATORY RECORDS
1954

TECHNICAL DIVISION

REACTION OF NITRIC ACID WITH DIISOPROPYL KETONE: PREPARATION AND IDENTIFICATION OF 2-NITRO 2, 4-DIMETHYL PENTANONE-3

OAK RIDGE NATIONAL LABORATORY
CENTRAL RESEARCH LIBRARY
CIRCULATION SECTION
4500N ROOM 175
LIBRARY LOAN COPY
DO NOT TRANSFER TO ANOTHER PERSON
If you wish someone else to see this report, send in name with report and the library will arrange a loan.
UCN-7969 (3 9-77)

AUTHOR
M.R. POSTON

[redacted]

OAK RIDGE NATIONAL LABORATORY

OPERATED BY
CARBIDE AND CARBON CHEMICALS CORPORATION
FOR THE
ATOMIC ENERGY COMMISSION
POST OFFICE BOX P
OAK RIDGE, TENNESSEE

[redacted]

[redacted]

ORNL-40
5-3-48

Oak Ridge National Laboratory

Technical Division

Chemical Process Development Section

This document consists 20 pages.
Copy 3 of 91 Series A.

ISSUED:

706-A Library

FINAL REPORT

Title

REACTION OF NITRIC ACID WITH DIISOPROPYL KETONE; PREPARATION AND IDENTIFICATION OF 2-NITRO 2, 4-DIMETHYL PENTANONE-3

Author

M. R. Poston

Abstract

Reaction of diisopropyl ketone with concentrated nitric acid produced a previously unreported solid nitroketone, 2-nitro 2, 4-dimethyl pentanone-3.

MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES

3 4456 0360242 0

Work by: M. R. Poston, B. I. V. Bailey, W. H. Baldwin

Secret Notebooks Nos.: CL-1321, CL-1613, CL-1618, CL-1728

Period of Work: 8-1-46 to 12-1-47

Date of Report: May 3, 1948

[redacted]

Date Received: 9/13/48

Date Issued: OCT 4 1948

[redacted]

[redacted]

Table of Contents

	Page No.
1.0 Introduction	3
2.0 Summary	5
3.0 Experimental	6
3.1 Preparation of 2-Nitro 2, 4-Dimethyl Pentanone-3	6
3.2 Identification of 2-Nitro 2, 4-Dimethyl Pentanone-3	8
3.21 Hydrolysis with NaOH	8
3.22 Identification of Pseudo Nitrole	9
3.23 Synthesis of 2-Nitro 2, 4-Dimethyl Pentanone-3	10
3.3 Properties of 2-Nitro 2, 4-Dimethyl Pentanone-3	12
3.31 Physical Properties	12
3.32 Effect on Uranium Distribution in Hexone	12
3.33 Effect on Gross Decontamination	13
3.4 Reactions of 2-Nitro 2, 4-Dimethyl Pentanone-3	14
3.41 Behavior with NaOH Solution	14
3.42 Reactions with Grignard Reagent	15
3.43 Reduction of 2-Nitro 2, 4-Dimethyl Pentanone-3	16
4.0 Bibliography	

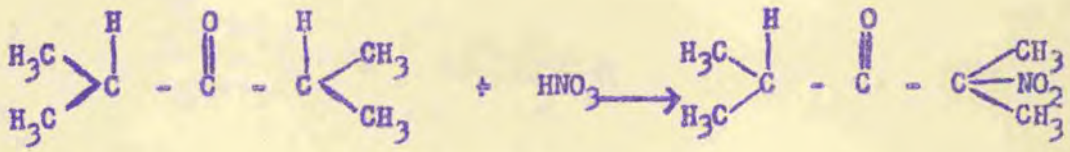
[redacted]

[redacted]

1.0 Introduction

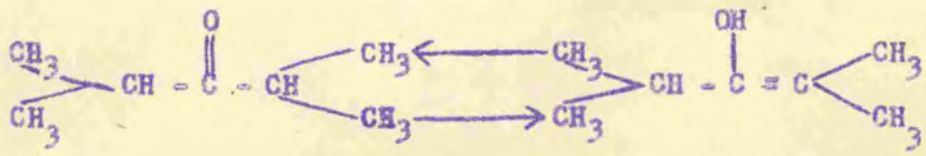
The existence of a solid reaction product from diisopropyl ketone and nitric acid was first reported when that solvent was being investigated as a medium for uranium extraction (1). At that time the reaction product was thought to be polymeric in nature.

The reaction between nitric acid and diisopropyl ketone is interesting in that the carbonyl linkage remains intact; thus:



The reaction of certain other ketones with nitric acid has been reported to yield nitrated fragments of the original ketone, e.g., diethyl ketone, methyl ethyl ketone, or ethyl propyl ketone has been reported to yield 1, 1-dinitroethane when treated with concentrated nitric acid (2). The oxidation of methyl isopropyl ketone with nitric acid has been shown to retain the carbonyl group in the formation of acetylisobutyryl (3). In this latter case, however, nitration of the ketone does not occur. The reaction of ethyl isopropyl ketone and nitric acid or ethyl isobutyl ketone and nitric acid has been reported to yield dinitroketones, with substitution occurring on the ethyl carbon atom adjacent to the carbonyl group (4). Previous work, therefore, would lead one to expect that any ketone containing a tertiary carbon atom would yield a nitration product other than the dinitro cleavage product mentioned above. It is well known that with hydrocarbons ease of nitration decreases in passing from a tertiary to a secondary to a primary group (5). In view of the fact that diisopropyl ketone could enolize in the following manner:

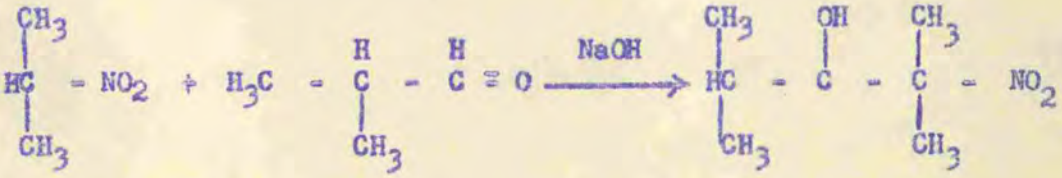
[redacted]



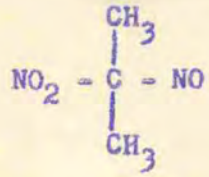
it is reasonable that the logical points of attack by nitric acid would be either the tertiary hydrogen or the double bond in the enol form.

2.0 Summary

The action of concentrated nitric acid on diisopropyl ketone was found to produce a white crystalline material with a camphor-like odor. This material was identified as 2-nitro 2, 4-dimethyl pentanone-3. Structure was established by identifying the products of hydrolysis by carbon, hydrogen, nitrogen and molecular weight determinations, and by synthesizing the nitroketone through synthesis and oxidation of the corresponding nitroalcohol. The nitroalcohol was prepared from 2-nitropropane and isobutyraldehyde according to the following reaction:



Upon refluxing 2-nitro 2, 4-dimethyl pentanone-3 in 10% NaOH and acidifying the resulting solution with dilute H_2SO_4 the following products were obtained and identified: 2-- nitropropane, acetone, and isobutyric acid. When the nitroketone was dissolved in cold NaOH by stirring at room temperature for several hours and the resulting solution carefully acidified a different decomposition product, 2 nitro 2 - nitroso propane:



was obtained.

The addition of 2-nitro 2, 4-dimethyl pentanone-3 to hexone was found to increase the extractability of fission products from a salted feed.

3.0 Experimental

3.1 Preparation of 2-Nitro 2, 4 Dimethyl Pentanone-3

The reaction between concentrated nitric acid and diisopropyl ketone was characterized by the evolution of brown fumes and heat. The intensity of the reaction increased in proportion to the amount of nitric acid present. It is believed that when the over-all acid concentration exceeds 3 molar the reaction should be attempted only in equipment designed for pressure reactions. In Table I below is given data for various acid concentrations. Yield is based on the reagent nitric acid.

Table I

Preparation of 2-Nitro 2, 4-Dimethyl Pentanone-3

Diisopropyl Ketone (Moles)	Nitric Acid (Moles)	Yield of Nitro Ketone (Moles)	Yield* of Crude Product (%)
11	1.4	0.38	27
11	1.9	0.48	25
11	2.3	0.77	33
11	2.6	0.95	37
11	3.9	1.48	38
2.1	0.95	0.35	37
2.2	3.5	0.28	8
2.2	4.1	0.35	9
2.2	5.5	0.39	7
2.2	6.9	0.64	9

* Based on HNO_3 employed in the reaction.

Experimental. 242 g(2.1M) of diisopropyl ketone and 60 g(0.95M) of 70% HNO_3 were placed together in a 500 ml. round bottom flask with two reflux condensers attached. The flask was warmed gently with an electric heating mantle until reaction was initiated and then the reaction vessel was surrounded by a cooling bath maintained at 30° C. After approximately five minutes when the reaction had subsided the cooling bath was removed and sufficient heat was applied to cause refluxing of the mixture. Refluxing was continued for one and one-half hours. The liquid was next transferred to a steam distillation apparatus and steam distilled until most of the organic phase had distilled over. The aqueous pot residue was cooled and 56 g. (0.35 Moles) of yellowish crystals were recovered. These crystals were purified by crystallizing from 42 ml of ethyl alcohol, yielding 45 grams (30% yield) of white crystals having a distinct camphor-like odor and melting point of 53.5° C. Further purification by recrystallization raised the melting point to 55° C. A sample of the nitroketone was submitted for analytical determinations. Results are tabulated in Table II.

Table II

C, H, N, and Molecular Weight Determinations*

Determination	Found	Calculated for $C_7H_{13}NO_3$
C	52.0	52.8
H	8.0	8.2
N	8.7	8.8
Mol. Wt.	144.	159.

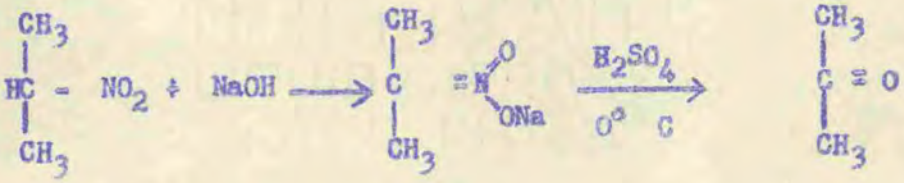
*Work by E. L. Will, Monsanto Laboratories, St. Louis, Missouri

3.2 Identification of 2-Nitro 2, 4-Dimethyl Pentanone-3

The nitroketone was identified by analyzing the decomposition products. When the structure of the compound was determined it was synthesized and a mixed melting point determined to confirm the structure.

3.21 Hydrolysis with NaOH

Approximately 1 mole (150 g.) of the nitroketone was added to 750 ml. of 10% NaOH and the solution was refluxed for 2 hours. When the solution was cooled and acidified with dilute H_2SO_4 a top layer separated. This material, (51 g.) was found to distill largely at 119° - 120° C. It was identified as 2 nitropropane by boiling point and by conversion to acetone as in the following (6):



The acetone above was converted to the 2, 4-dinitrophenyl-hydrazone which had a melting point of 125° - 126° C. A mixed melting point was determined using this derivative and one prepared from c.p. acetone. Found: 125° - 126° C.

The lower layer, or aqueous, was extracted with ethyl ether and the ether was removed by distillation. Seventy-seven grams of liquid boiling between 149° and 153° C was obtained. This material was identified as isobutyric acid by boiling point and by preparation of the following derivatives: p - phenyl phenacyl ester, m.p., 88° - 89.5° C, and p - bromophenacyl ester, m.p., 75° - 77° C. In both cases mixed melting points were determined using derivatives prepared from known isobutyric acid. Found: p - phenyl phenacyl ester mixed m.p., 88° - 89° C; p - bromophenacyl ester mixed m.p., 75° - 77° C.

3.22 Identification of the Pseudo Nitrole

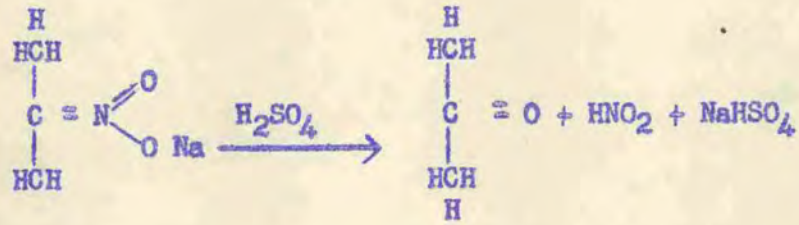
Fifty grams of the nitroketone were added to 275 ml of 10% NaOH and the mixture was agitated for 4 hours at room temperature to yield a homogeneous solution. This basic solution was cooled to 10° C in an ice bath and 10% H_2SO_4 was added dropwise while stirring until the solution was acid to litmus. White crystals immediately formed in the cold acid solution and were filtered off and found to weigh 5.2 g (yield 15%). These crystals exhibited typical properties of a nitroso compound: insoluble in water; dissolved to a blue solution in ether, benzene, or ethanol; melted from a white solid to a blue liquid. The melting point of the unpurified crystals was 62.5 - 64° C (uncor.). Three successive crystallizations from ethanol yielded material melting at 67.5° - 68.5° C (uncor.), 69.5° - 70.5° C (uncor.) and 71.5° - 72.0° C (uncor.).

2 - nitroso 2 - nitro propane (Beilstein I, p. 116) was prepared by adding H_2SO_4 to a solution of 2-- nitropropane in dilute NaOH containing sodium nitrite. This unpurified material had a m.p. of 65° - 66° C. A mixed melting point of this known 2 - nitroso 2 - nitro propane and the 62.5 - 64° crystals from above was determined to be 62° - 65° C.

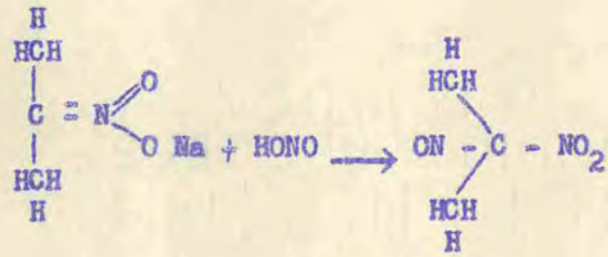
Further evidence of the identity of this decomposition product was obtained by oxidation of the 2 - nitroso 2 - nitro propane to 2, 2 - dinitro propane. This was accomplished by adding 5 g. of chromic acid in small portions with constant stirring and steam distilling the resulting solution after making basic with NaOH (7). Less than 1 g. (20% yield) of the dinitro compound, m.p. of 47° - 47.5° C, was obtained. A mixed melting point with these crystals and the dinitro propane crystals obtained from the nitroketone was found to be 46.5° - 47.5° C.

The preparation of the 2-nitroso 2-nitro propane - or pseudo nitrole - and the oxidation of this compound to the dinitro propane are understood to proceed as follows:

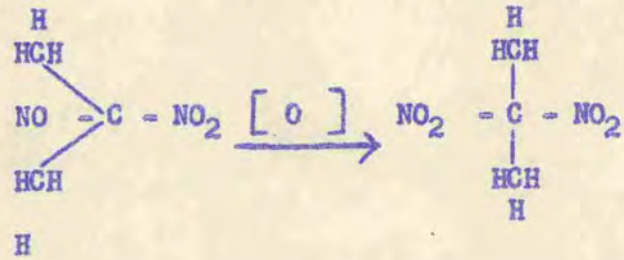
(1)



(2)



(3)

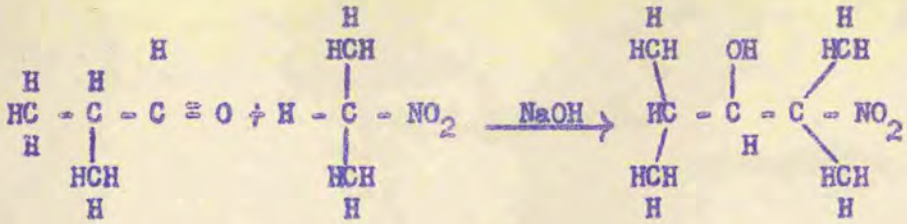


Since steps (1) and (2) occurred simultaneously during the acidification of the basic solution the low yield of the nitroso compound may be explained by the conversion of at least one-half of the 2-nitropropane to acetone, during which step nitrous acid was produced. It was the action of this nitrous acid on unreacted 2-nitro propane which produced the pseudo nitrole.

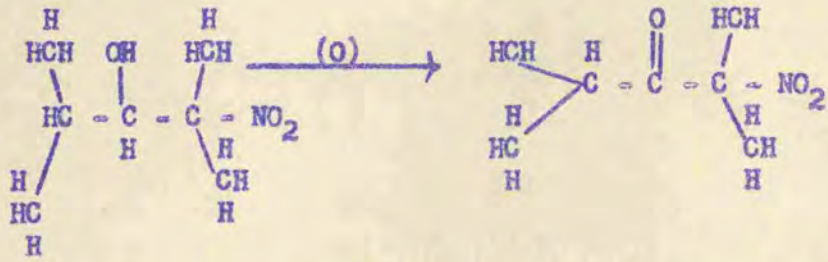
3.23 Synthesis of 2-Nitro 2, 4-dimethyl Pentanone-3

A method for preparing a nitro alcohol from a nitro paraffin and an aldehyde has long been known (8). It was decided to prepare 2-nitro 2, 4-dimethylpentanol-3 which could then be oxidized to the nitroketone. The required materials for this synthesis, then, were isobutyraldehyde and 2-nitro-propane reacting as follows:

(1)



(2)



A solution of 72 g. (1 Mole) of isobutyraldehyde and 89 g. (1 Mole) of 2-nitropropane was dissolved in 75 ml. of ethyl alcohol. One gram of NaOH dissolved in 5 ml. of water was added, and the mixture was allowed to stand at room temperature for three days. At this point an excess of concentrated hydrochloric acid was added and the precipitated NaCl was filtered off. The filtrate, blue in color, contained unreacted isobutyraldehyde, 2-nitropropane, ethanol, and 17 grams of the nitroalcohol, which was recovered by vacuum fractionation. The nitroalcohol was found to boil at 95°C (uncor.) at 10 mm. It is believed that the low yield, 11%, could have been increased by agitation of the reaction mixture.

Seventeen grams of the nitroalcohol obtained above were added to 17 grams of $Na_2Cr_2O_7$ in 10 ml. of water, held in a water bath at 25°C. Over a period of eight hours a solution of 11 ml. of concentrated sulfuric acid in 5 ml. of water was added in small portions. Continuous stirring was maintained during the acid addition. Stirring was continued for an additional 16 hours after which an equal part of water was added. The solution was next extracted with ethyl ether and the ether distilled off to give 2.6 grams (yield: 15%) of 2-nitro 2, 4-dimethyl pentanone-3. After crystallizing from a water-methanol mixture a product was obtained with a melting point of 54° - 56°C. A mixed melting point was run with this material and nitroketone prepared from diisopropyl

ketone. Found: 54° - 56.5° C.

3.3 Properties of 2-Nitro 2, 4-Dimethyl Pentanone-3

When first recovered from the nitration of diisopropyl ketone the crude nitroketone was yellow in color. Upon purification by crystallization or sublimation white crystals were obtained. Methanol and ethanol were found to be satisfactory solvents for crystallizing the product.

Dissolution of the nitroketone in dilute NaOH was accomplished only with prolonged agitation or with the application of heat. In Table III is presented data concerning solubility of the nitroketone at room temperature with agitation. Ten grams of crystals were added to 100 ml. of 10% NaOH. Solubility was determined by filtering off and weighing undissolved solid.

Table III

Solubility of 2-Nitro 2, 4-Dimethyl Pentanone-3 in 10% NaOH

Time of Stirring	Wt. Dissolved
60 min.	6.7 g.
120 min.	9.5
180 min.	10 g. (complete)

3.31 Physical Properties

When pure, 2-nitro 2, 4-dimethyl pentanone-3 is white in color, it possesses a camphor-like odor. This material has a tendency to sublime at room temperature. It is soluble in ether, acetone, alcohol and benzene, and insoluble in water. The melting point of pure nitroketone was found to be 55°C, and the boiling point of pure material was determined to be 189°-190° C/745 mm. and 72° C/10 mm. Distillation of the nitroketone at atmospheric pressure was accomplished without observable decomposition.

3.32 Effect on Uranium Distribution in Hexone

A scouting experiment was conducted to determine what effect small concentrations of the nitroketone would have on uranium distribution in hexone. The aqueous solution for this experiment contained the following:

0.5M $Al(NO_3)_3 \cdot 9H_2O$

0.2M HNO_3

10 g. U/liter

Hexone containing varying concentrations of the nitroketone was used to extract the above aqueous at room temperature. Results are presented in Table IV.

Table IV

Effect of Nitroketone on U Distribution in Hexone

Conc. of Nitroketone in Hexone	U Dist. Coeff. (aq./org.)
None	4.35
0.1M	4.65
0.5M	5.80
1.0M	6.40
1.5M	7.45

3.33 Effect on Gross Decontamination

An experiment similar to that described in Section 3.32 was conducted to determine the effect on gross decontamination when the nitroketone was added to hexone. A higher salting agent concentration was used in this experiment and a slight effect on activity distribution was observed. The aqueous feed was made up as follows:

2.5M $Al(NO_3)_3 \cdot 9H_2O$

0.2M HNO_3

Dissolver solution spike-9 months old.

Hexone containing varying concentrations of the nitroketone was used to extract

the above aqueous, and a count was made of the gross activity in each phase. Results are contained in Table V.

Table V

Effect of Nitroketone on Gross Activity Distribution in Hexone

Conc. of Nitroketone in Hexone	Gross Activity D.C.(aq./org.)
None	10
0.1M	11
0.5M	6.7
1.0M	5.4
1.5M	5.7

3.4 Reactions of 2-Nitro 2, 4-Dimethyl Pentanone-3

The manner in which decomposition products were obtained by refluxing the nitroketone with NaOH and acidifying the resulting solution led to an investigation of the behavior of the nitroketone with NaOH. It is known that tertiary nitroparaffins will not form sodium salts whereas those nitroparaffins which contain hydrogen attached to the carbon atom holding the NO_2 group will dissolve in alkali to form salts (9). No evidence was obtained that a sodium salt of the nitroketone was obtained.

3.41 Behavior with NaOH Solution

When the NaOH solutions of nitroketone obtained by refluxing with heat or agitating at room temperature were acidified with dilute H_2SO_4 decomposition products were obtained (Section 3.2). In no case was the original nitroketone recovered upon acidification. It was believed that a milder acidifying agent might be instrumental in the recovery of the original nitroketone from the alkali solution. Dilute acetic acid was used for this purpose but the results as reported below indicate that essentially the same type of decomposition products were obtained.

Experimental. Ten grams (0.063 Moles) of nitroketone crystals were dissolved in 50 ml. of 10% NaOH by stirring at room temperature for two hours. The alkali solution was held in a bath at 10° C while 10% acetic acid was added dropwise with stirring. When the solution was acid to litmus it was extracted with ethyl ether and the ether was removed by distillation. The resulting solution, 9.6 grams, was found to distill as follows:

Amount (ml)	Temperature (°C)
2	105
5	118
6	123
10	147
12	160

From the distillation range it was concluded that the recovered product consisted principally of the cleavage products, 2-nitro paopane and isobutyric acid.

3.42. Reaction with Zerewitinof Reagent

To confirm the structural composition of the nitroketone, a study was made of the reaction between Zerewitinof reagent and the nitroketone. Zerewitinof reagent, methyl Grignard reagent in a high boiling ether, is available commercially. A Grignard machine embodying improvements by Lauer was constructed (10). The experimental technique for this determination was as follows. A weighed sample of the nitroketone was added to the reaction vessel and the entire system was flushed with dry nitrogen gas for a period of twenty minutes. Next the gas measuring buret was adjusted so that the reaction vessel was at a pressure less than atmospheric and a reading was made of the mercury level. A carefully measured amount of Zerewitinof reagent was then charged to the reaction vessel by use of a medical syringe and a hypodermic

needle. Agitation was accomplished by the use of a glass-coated magnet in the reaction vessel. After ten minutes reaction time a second reading of the mercury level was made and an excess of water was added from the syringe. Upon the completion of the evolution of gas from this addition a third and final reading was taken. The results from this determination are given in Table VI below:

Table VI

Reaction Between Nitroketone and Zerewitinof Reagent

Sample		Reagent	Gas	H_2O Added	Gas Generated		Reagent Combined by
G.	Millimoles	Ml.	Ml.	Millimoles	Ml.	Millimoles	Sample(Mole/Mole)
		2.0		110	9.6	0.428	
		2.0		280	9.2	0.410	
0.12	0.755	2.0	None	110	None		
0.12	0.755	3.0	None	110	None	0.049	0.77
0.12	0.755	4.0	None	110	None	0.24	0.80

By reference to Table VI it is seen that slightly less than one mole of reagent was consumed by each mole of the nitroketone. The experimental finding was believed to be sufficiently near the calculated value to prove the existence of the carbonyl group in the nitroketone. The discrepancy between the experimental and calculated values may have been due to one or more of the following:

(1) No solvent was used for the nitroketone;

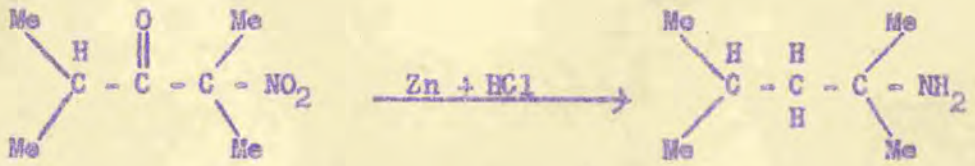
(2) The reaction vessel was not heated during reaction;

(3) The presence of the nitro group may have influenced the reaction with Grignard reagent.

3.43 Reduction of 2-Nitro 2, 4-Dimethyl Pentanone-3

A Clemmensen reduction of the nitroketone would be expected to proceed as follows:

[redacted]



The expected product, 2-amino 2, 4-dimethyl pentane (Beilstein IV, p. 195) has the following properties: boiling point 121-22°C, density 0.7720, refractive index at 30°C, 1.4009.

A number of attempts were made to subject the nitroketone to Clemmensen reduction. The products of reduction were not identified and it is believed that one or more unexpected reactions occurred. The catalytic reduction of some gamma nitroketones have been reported to result in a succession of reduction and condensation reactions formed simultaneously (11). Clemmensen reduction of the nitroketone was attempted using three different sets of conditions: (a) no solvent, (b) an immiscible solvent, toluene, and (c) a miscible solvent, ethanol (12). This work is described below.

Experimental. (a) To 120 g. of amalgamated zinc added 75 ml. water, 100 ml. concentrated HCl, and 50 g. of the nitroketone. This mixture was refluxed for 26 hours during which time an additional 100 ml. of acid was added. The solution was cooled and 40% NaOH solution added until no turbidity remained. The basic solution was extracted with ether and upon removing the ether by distillation 22 g. of liquid was obtained which distilled as follows:

Amount (% Off)	Temp. (°C)
4	75
20	104
40	160
60	190
80	210
96	220

[redacted]

(b) Fifty grams of nitroketone were added to 100 g. of amalgamated zinc, 100 ml. of toluene and 175 ml. of concentrated HCl. The mixture was refluxed gently for 24 hours after which it was made alkaline and extracted as in (a) above. After the ether and toluene were removed through a small distillation column the temperature rose rapidly to 170° C and solid nitroketone began freezing out in the condenser. The results indicate that little of the nitroketone was affected by reducing under this set of conditions.

(c) To 100 g. of zinc amalgam was added 40 ml. water, 100 ml. HCl and 20 ml. of ethyl alcohol. This mixture was refluxed and over a period of 6 hours a solution of 50 g. of nitroketone in 115 ml. of ethanol was added in small portions. The solution was made basic and extracted as above. This produced 41 g. of liquid which was fractionated from a small laboratory column as follows:

Charge: 55 ml.

Amount (% Off)	Temp. (°C)
9	60
18	88
23	100
33	110
51	120
60	120
70	125

The cut boiling between 110 and 121°C was used in an attempt to prepare an HCl derivative. Only a white cloudiness was obtained. Of the three sets of conditions used, condition (c) above gave the most satisfactory results.

[redacted]

4.0 Bibliography

1. MonC-145, Solvent Extraction for Uranium Recovery from Homogeneous Pile Solution, W. H. Baldwin, August 23, 1946.
2. Sidgwick, Taylor and Baker, The Organic Chemistry of Nitrogen, Clarendon Press, Oxford, 1945, p. 243.
3. Aston, J. G., Menard, D. F., and Mayberry, M. G., J. Am. Chem. Soc. 54, 1530, (1932).
4. Fileti, M., and Ponzio, G., J. Prakt. Chem. 55, 195 (1897).
5. Degering, E. F., Bordenca, C., and Gwynn, B. H., An Outline of Organic Nitrogen Compounds, John S. Swift Co., Cincinnati, Ohio 1942, p. 65.
6. Hass, H. B., Riley, Elizabeth F., Chem. Rev. 32, 373 (1943).
7. Meyer, V., Annalen der Chemie, 180, 147.
8. Henry, Comp. rend., 120, 1265 (1895).
9. Sidgwick, Taylor, and Baker, op. cit., p. 231.
10. Fieser, L. F., and Fieser, Mary, Organic Chemistry, D. C. Heath and Co., Boston, 1944, p. 211.
11. Kohler, E. P., and Drake, N. L., J. Am. Chem. Soc. 45, 2144 (1923).
12. Adams, Roger and Others, Organic Reactions, John Wiley and Sons, New York, 1944, p. 166.

[redacted]