THE IDENTIFICATION

OF

NITROPARAFFINS

THE IDENTIFICATION OF NITROPARAFFINS

By

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HISTORICAL BACKGROUND

The nitroparaffins were first produced by Victor Meyer (18) in 1872 by heating silver nitrite and alkyl halides to high temperatures in sealed tubes. Kolbe (17) in the same year prepared nitromethane by treating chloroacetic acid with potassium nitrite, forming nitroacetic acid as an intermediate compound. The first intensive study of the nitration of paraffin hydrocarbons was done in the years between 1892 and 1907, but interest soon lagged because of the difficulty and cost of preparing the pure compounds. In spite of the situation the study of preparing the nitroparaffins was taken up in 1930 by Haas and his co-workers--Hodge and Vanderbilt--(9) at Purdue University. They were successful in arriving at a method of nitrating the lower aliphatic hydrocarbons by the use of nitric acid in the vapor phase. The resulting nitroparaffins are colorless liquids with densities close to that of water and odors resembling that of chloroform. As solvents for pyroxylin lacquers, cellulose acetate, and Vinylites they are difficult to excel. The accessibility and low cost of the nitroparaffins, brought about by vapor phase nitration by Commercial Solvents Company in its plant at Peoria, Illinois, has led to the synthesis of hundreds of new compounds from the nitroparaffins (6).

The means of identification of the nitroparaffins now used depends primarily on their physical constants. At Purdue University the products of nitration were identified (9) in the following manner:

> "Nitromethane was identified by its boiling point, 101°C, and the formation of the potassium salt of methazonic acid on treatment with concentrated potassium hydroxide.
>
> "2-Nitropropane was identified by its physical constants, by

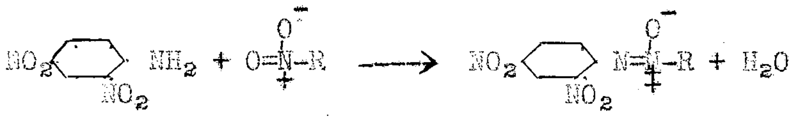
> conversion to the pseudonitrole, and by a Dumas nitrogen determination.
>
> "Nitroethane, 1-nitropropane, 1-nitrobutane, and 2-nitrobutane were identified by their physical constants and starting materials."

The purpose of this investigation was to find suitable crystalline derivatives for the identification of nitromethane, nitroethane, 1-nitropropane, and 2-nitropropane. Derivatives were sought with three objectives in mind; to make derivatives with a suitable spread of melting points by the same procedure on each nitro compound, to select methods that do not involve excessive time or equipment, and to limit the reagents used to those whose availability and cost permit them to be found in all qualitative organic laboratories.

Two methods of approach were made; the first involved the nitro group, the other the active hydrogen on the carbon atom adjacent to the nitro group.

REACTIONS OF THE NITRO GROUP

An attempted reaction between the nitroparaffin and 2,4-dinitroaniline in an effort to split out water to form a 2,4-dinitrophenylazoxyalkane by the reaction:



was unsuccessful, the reagents being recovered unchanged.

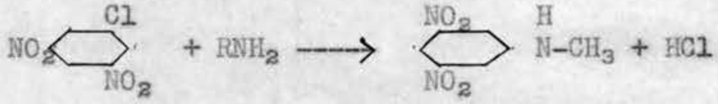
The use of a Grignard reagent was considered but rejected after it was found that Wang (24) reported a multiplicity of products from the interaction of nitroparaffins and arylmagnesium halides.

The nitro groups of both aliphatic and aromatic compounds have long been known to give amines upon vigorous reduction,

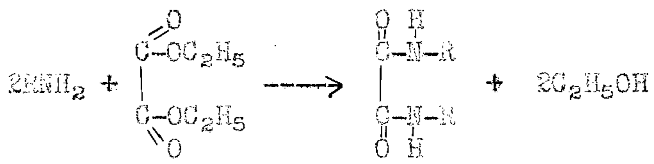
$$RNO_2 \xrightarrow{H_2} RNH_2$$

and many methods have been used to accomplish this (13). In this work successful results were obtained by carrying out the reduction by adding concentrated hydrochloric acid intermittently in small quantities to granular zinc in the nitroparaffins. The corresponding amines were liberated from their hydrochlorides by the addition of sodium hydroxide. The free amines, although very volatile, are quite soluble in water, and do not escape from solution if it is kept cool. Efforts were made to produce derivatives using benzoyl chloride and benzenesulfonyl chloride on the freshly liberated amine, but suitable products were not obtained. The failure may have been due to the presence of the very concentrated salt solution containing zinc hydroxide, much of which did not dissolve in excess sodium hydroxide. p-Nitrobenzoyl chloride gave a deep red coloration to the solutions in each case, but no solid product was formed.

Valton (26) in 1924 suggested detecting methylamine in an ammonia solution by distilling the amine and water into an alcoholic solution of 2,4-dinitrochlorobenzene. The methylamine reacts preferentially to give a precipitate of N-methyl-2,4-dinitroaniline:



This distillation method was adopted for identifying the amines resulting from the reduction of the nitroparaffins. After the amines had been freed from their hydrochlorides, the solution was distilled into reagents that would yield suitable derivatives. When 2,4-dinitrochlorobenzene was used in the receiver, solid derivatives, the alkyl-2,4-dinitroanilines, were obtained for all four of the reduced nitroparaffins. Saturated aqueous and alcoholic solutions of picric acid, so often used to give derivatives of amines, formed picrates that would not crystallize from the solutions. Upon evaporation of the solvent the picrates could be isolated, but yields were poor and the products impure; hence, such a procedure is not considered satisfactory. Picryl chloride as the reagent did not produce any insoluble product. Diethyl oxalate and phenyl isothiocyanate when reacted with the amines formed the sym-dialkyloxamides and sym-alkylphenylthioureas respectively:



These products, obtained in good yields, are solids and have definite and reproducible melting points.

Meyer showed that by gradual reduction of a nitroparaffin an N-alkylhydroxylamine is formed as an intermediate product (21),

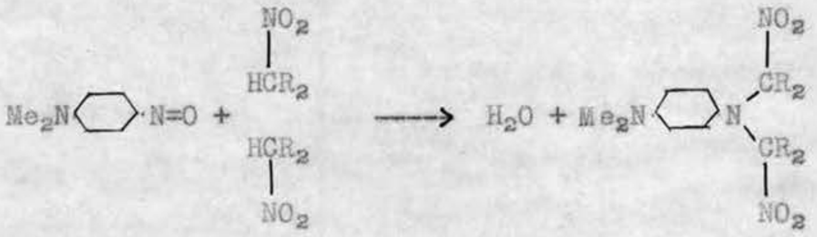
$$CH_3NO_2 \xrightarrow{H_2} CH_3NHOH + H_2O$$

These alkylhydroxylamines are known to combine with picric acid and other amine precipitants to form crystalline salts. Although this method for forming derivatives of the nitroparaffins was not investigated, the reaction is mentioned as a possibility for future work.

Thus the procedure that seems best for the identification of the nitroparaffins by reaction of the nitro group is the formation of the amine, followed by the distillation of the amine into 2,4-dinitrochlorobenzene, diethyl oxalate, or phenyl isothiocyanate. The new development is merely an organization of known procedures to give one continuous method of forming the derivatives.

REACTIONS OF THE ACTIVE HYDROGEN

Nitromethane was refluxed with p-nitrosodimethylaniline in an attempt to combine them in the following manner:

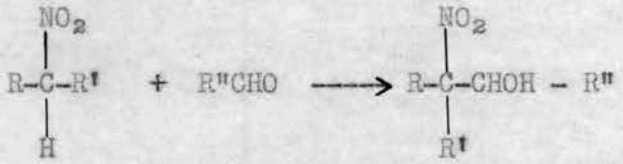


but the only product was a black tarry mass. The same results were obtained when pyridine was used as a catalyst.

Metatheses with high-molecular-weight alkyl halides were tried using such reactants as phenacyl bromide, p-bromophenacyl bromide, and p-nitrobenzyl chloride. Refluxing these halides fifteen to thirty minutes with the sodium salt of nitromethane, nitroethane, 1-nitropropane, or 2-nitropropane yielded no solid organic products in any instance.

Using the procedure for coupling chloroacetic acid with phenols, an attempt was made to react chloroacetic acid with the sodium salt of the nitroparaffins. A reaction was believed to have taken place, but the products were so soluble in water that the procedure was considered useless for this work, and no effort was made to isolate them.

Condensation of the nitroparaffins with the carbonyl group of ketones and aldehydes is not a new reaction, for Henry (10) in 1895 found that nitroalcohols could be prepared from nitroparaffins and aliphatic aldehydes. In general the aldehyde-nitroparaffin condensation is of the aldol type, the active hydrogen always going to the oxygen of the aldehyde and the radical containing the nitro group to the carbonyl carbon:



$$R-\underset{H}{\overset{NO_2}{C}}-R' + R''CHO \longrightarrow R-\underset{R'}{\overset{NO_2}{C}}-CHOH-R''$$

These reactions are not spontaneous, but must be promoted by a catalyst such as sodium methoxide, sodium ethoxide, ethylamine, or methylamine. Such reactions were studied extensively by Vanderbilt and Hass (25) for they allowed nitroethane, 1-nitropropane, 2-nitropropane, 1-nitrobutane, 2-nitrobutane, and 2-methyl-1-nitropropane to condense singlely with formaldehyde, acetaldehyde, and butyraldehyde. Nitromethane was omitted from their work as it had been previously studied by Henry (10) and Hofwimmer (11). The nitroalcohols resulting from the above reactions are liquids or solids very difficult to crystallize; hence, they were not considered as possibilities in this work.

The nitroalcohols formed from aliphatic aldehydes and primary nitroparaffins readily split off water and form the corresponding nitroölefins:

$$RCHNO_2CHOHR' \longrightarrow RCNO_2 = CHR' + H_2O$$

This type of reaction is very difficult to avoid (12).

With such information in mind, attempts were made to react the nitroparaffins available for this problem with benzaldehyde, cinnamaldehyde, salicylaldehyde, and piperonal, in the presence of sodium methoxide. Equal molar amounts of each nitroparaffin and cinnamaldehyde were shaken together with a few drops of sodium methoxide. The same procedure was repeated using salicylaldehyde in place of cinnamaldehyde. When the solutions were allowed to stand for one week, no solid product was formed; and when the solution was poured into water, an oil separated which would not crystallize.

Equimolecular amounts of piperonal and the nitroparaffins were combined in a little alcohol, a few drops of sodium methoxide were added, and the mixture was allowed to stand three days. No solid product formed in the mixture. When it was poured into water an oil separated which would not crystallize. The same procedure was carried out using equivalent weights of sodium methoxide,piperonal, and nitroparaffin. The mixture was poured into water, in which it was completely soluble, and the solution acidified with dilute acid. A non-crystallizable oil separated.

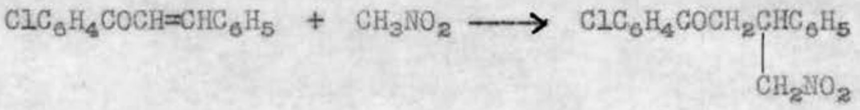
According to a procedure in Houben (14), benzaldehyde will condense with the sodium salt of nitromethane to give upon acidification ω-nitrostyrene, a solid.

> "Mix equimolar amounts of nitromethane and benzaldehyde in a little alcohol. Add an equimolar amount of concentrated sodium methoxide dropwise, keeping the mixture cool. When the mixing is complete, an addition of dilute hydrochloric acid precipitates ω-nitrostyrene. Recrystallization from alcohol yields yellow needles melting at 58°C."

The procedure was carried out but an oil was the only product obtained.

When the other nitroparaffins were substituted for nitromethane, an oil separated in each instance. Refluxing the reagents fifteen to thirty minutes had no effect on the appearance of the product, which was still an oil.

The reaction of the nitroparaffins with the carbonyl group of ketones is similar to that with the corresponding group of aldehydes. α-β- Unsaturated ketones condense with nitromethane to give γ-nitroketones. An example of this is the reaction of sodium nitromethane with benzal-p-chloroacetophenone (16) in hot ethanol:



$$ClC_6H_4COCH{=}CHC_6H_5 + CH_3NO_2 \longrightarrow ClC_6H_4COCH_2\underset{\displaystyle CH_2NO_2}{\underset{|}{C}}HC_6H_5$$

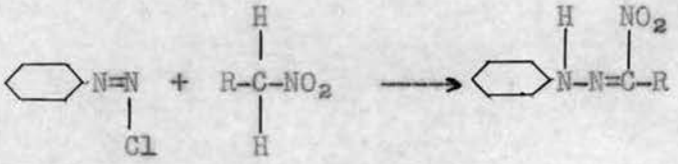
Kohler also reacted nitroparaffins with benzalacetophenone (15) and obtained solid products with nitromethane and 1-nitropropane; no solid derivatives were formed with nitroethane or 2-nitropropane. The same results were obtained in this work.

Cyclohexanone reacts with nitromethane (5), but does not give a solid product. The same results were obtained when equimolecular amounts of each of the other nitroparaffins and cyclohexanone were allowed to stand for one week. A trace of sodium methoxide was used as a catalyst.

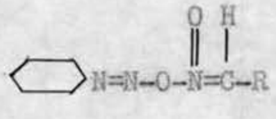
Phenyl isocyanate reacts with the sodium salt of a nitroparaffin (3, 22, 23) to yield a variety of products. s-Diphenylurea and triphenylbiuret can be isolated from all the reaction mixtures of phenyl isocyanate with nitromethane, nitroethane, 1-nitropropane and 2-nitropropane. This procedure was varied slightly by using pyridine as a catalyst instead of the sodium salt. An exothermic reaction took place when the materials were mixed. After standing at room temperature for three hours, a crystalline solid separated in all four cases. The solids upon recrystallization from ethanol were found to be the same compound, s-diphenylurea, which was identified by its melting point and consideration of the mechanism by which it formed (7). Other derivatives were no doubt present, but a separation would be too difficult to use in this identification.

No evidence of a reaction was noted nor did a product separate when phenyl isothiocyanate was treated with a nitroparaffin in the absence or presence of pyridine as a catalyst.

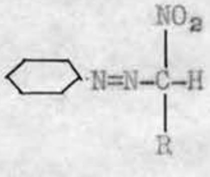
Primary and secondary nitroparaffins couple with diazonium salts (1, 19, 20) according to the reaction (using diazotized aniline as an example):



This structure for the product formed is the accepted one, as it is based upon analogous products obtained by reacting other compounds possessing an active hydrogen with diazonium salts. Other structures have been proposed (4):

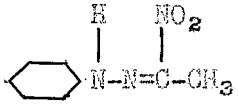


or



but it is more probable that these are intermediate compounds. Bamberger suggested naming the compounds as aldehyde derivatives (2).

For example nitroacetaldehydephenylhydrazone has the formula:



$$C_6H_5-\overset{H}{\overset{|}{N}}-N=\overset{NO_2}{\overset{|}{C}}-CH_3$$

Such naming does not clearly define the structure, for the name nitroacetaldehyde should be reserved for NO_2CH_2CHO.

The sodium salt of nitromethane reacting with diazotized aniline yields a multiplicity of products (3); however, the nitroethane salt gives a yellow solid, 1-nitropropane an orange solid, and 2-nitropropane an oil.

In this work the sodium salts of the nitroparaffins were treated with the diazonium salts derived from aniline, p-toluidine, p-nitroaniline, and β-naphthylamine. Nitroethane and 1-nitropropane gave solid products with diazotized p-toluidine; nitroethane, 1-nitropropane, and 2-nitropropane yielded solids with the diazonium salt derived from β-naphthylamine. With diazotized p-nitroaniline and each of the sodium salts of the nitro compounds, solid derivatives were obtained.

Nearly all of these compounds resulting from the coupling are brilliantly colored crystalline substance with sharp melting points.

EXPERIMENTAL

REDUCTION OF THE NITROPARAFFINS AND REACTIONS OF THE PRODUCTS

Approximately 10 grams of granular zinc and 4-6 ml of the nitroparaffin were placed in a 50 ml Erlenmeyer flask and the flask was connected to a reflux condenser. Concentrated hydrochloric acid was added in small quantities, approximately 1 to 2 ml at a time--just enough to keep up a vigorous evolution of hydrogen. The heat of reaction is sufficient to bring about proper refluxing. Complete reduction was assured by the disappearance of the top layer (the nitroparaffin). When cool, the solution was diluted with 5-10 ml of water and placed in an ice bath. Concentrated sodium hydroxide (35-40%) was added, but in small quantities so as to prevent the solution from becoming too hot. If the solution becomes too warm, the amine, liberated from its hydrate, escapes from solution. The addition of the sodium hydroxide was continued until the precipitate of zinc hydroxide nearly or completely dissolved. The material was transferred to a 125 ml distilling flask connected to a condenser. Approximately 10-20 ml of the amine-water solution was distilled into the reagent chosen, 2,4-dinitrochlorobenzene, diethyl oxalate or phenyl isothiocynate. Two grams of 2,4-dinitrochlorobenzene, in just enough alcohol to dissolve it, was a satisfactory reagent for producing the N-alkyl-2,4-dinitroanilines. When diethyl oxalate or phenyl isothiocyanate were used, the amine-water distillate was directed into 1.5 to 2 ml of the reagent itself. The N-alkyl-2,4-dinitroanilines, the sym-dialkyl oxamides, and the alkyl-phenylthioureas were recrystallized from hot ethanol. Their melting points were in close agreement with the ones given in literature. (see Table I).

COUPLING OF THE NITROPARAFFINS WITH DIAZONIUM SALTS

The diazonium salts of aniline, p-toluidine, p-nitroaniline and β-naphthylamine were prepared in the usual manner.

To 8 ml of the nitroparaffin in a 125 ml flask approximately 12 ml of concentrated sodium methoxide were added in small quantities while the flask was kept cool in an ice bath. A failure to note the odor of the nitroparaffin is a good indicator as to whether or not sufficient sodium methoxide has been added. To the salt of the nitroparaffin an equimolar amount of the freshly prepared diazonium salt solution was added, and the mixture was shaken vigorously. Occasionally small additional amounts of sodium methoxide were needed to bring about a complete solidification of the product. The product was isolated by filtration and washed with water containing a little hydrochloric acid to destroy any sodium salt that might have been present. The resulting compounds were dried and recrystallised from ethanol or an ethanol-water mixture. The crystals were then dried and melting points taken.

RESULTS

Table I

Derivatives of the Amines Obtained from Nitroparaffins

Original Nitroparaffin	Melting points of 2,4-dinitrochlorobenzene derivatives		Melting points of diethyl oxalate derivatives		Melting points of phenyl isocyanate derivatives	
	Author's work	Literature*	Author's work	Literature*	Author's work	Literature*
Nitromethane	174	175.5	210	212	112.5	113
Nitroethane	111	113	176	179	107	106
1-Nitropropane	96	95	162	162	62	63
2-Nitropropane	91	94	212	213	102	101

* Literature values taken from Beilstein, "Handbuch, der Organischen Chemie," 4th edition, Published by Springer, Berlin.

All temperatures measured in degrees Centigrade.

Table II

Results of Addition and Coupling Reactions

Reagent	Nitro-methane	Nitro-ethane	1-Nitro-propane	2-Nitro-propane
2,4-Dinitroaniline	----no visible effect noticed in any case			
p-Nitrosodimethylaniline	black tar	black tar	--not attempted --	
Phenacyl bromide	oil	oil	oil	oil
p-Nitrobenzyl chloride	oil	oil	oil	oil
p-Bromophenacyl bromide	oil	oil	oil	oil
Chloroacetic acid	---products all water soluble --------			
Benzaldehyde	oil	oil	oil	oil
Cinnamaldehyde	oil	oil	oil	oil
Salicylaldehyde	oil	oil	oil	oil
Piperonal	oil	oil	oil	oil
Cyclohexanone	------no product isolated ------------			
Benzalacetophenone	103*	oil	167*	no product
Phenyl isocyanate	--s-diphenylurea isolated in all cases--			
Phenyl isothiocyanate	--------no visible reaction------------			
Diazotized aniline	oil	OY needles** m. p. 141*	O needles** m. p.97-98	oil
Diazotixed p-toluidine	oil	YO needles** m. p. 157	OR needles** m. p.88-89	oil
Diazotized p-nitroaniline	OR, shade1** crystals m. p. 159	OY needles** m. p. 157	OR needles** m. p. 139-40	Y needles** m. p. 104
Diazotized β-naphthylamine	oil	OR needles** m. p. 159	OR needles** m. p. 138	OY, tint 1** needles m. p. 73-4

*Melting points agree with those found in literature

**Colors cited are so named by comparison with color chart in Mulliken, "Identification of Pure Organic Compounds," Vol. I, John Wiley and Sons, Inc., New York, 1904.

DISCUSSION OF RESULTS

The identification of the amines produced by the reduction of the corresponding nitroparaffin is relatively simple as the dialkyl oxamides, the alkylphenylthioureas, and N-alkyl-2,4-dinitroanilines are readily precipitated. The spread of melting points is not as wide as might be desired, but with such a procedure two or even all three of the derivatives might be made from the same distillation. In this manner an excellent check could be made. If only one type of derivative is to be made, the author would suggest the use of 2,4-dinitrochlorobenzene as the reagent.

From the results of the reactions between phenacyl bromide, p-nitrobenzyl chloride and p-bromophenacyl bromide with the sodium salt of the nitroparaffins, it can be concluded that the nitro compounds cannot be identified as solids.

The Knoevenagel reaction can be regarded as unsuitable for identification work as the final products of aldehyde and ketone condensations with the nitroparaffins were not solids.

The diazonium couplings gave products that might possess the properties of dyestuffs, although this possibility was not investigated. It was also found that these products were sensitive to alkali, turning bright red under alkaline conditions; hence they might be used as indicators.

Nitromethane was the only one of the nitroparaffins that could not be identified by coupling with diazonium salts. Nitroethane, 1-nitropropane, and 2-nitropropane, when they did couple with diazonium salts, gave a very suitable spread in the melting points of the products.

Nitromethane was abnormal in its behavior toward most of the reagents used in this work, although with benzalacetophenone the interaction was rapid and a clean product was isolated. This abnormality is also notable in other reactions of nitromethane. 2-Nitropropane, the only secondary nitro compound studied, was usually slower in its reactions than the primary compounds. Nitroethane and 1-nitropropane were more predictable in their reactions and gave several more diazonium couplings than did the other two nitroparaffins.

SUMMARY

Two methods for the identification of nitromethane, nitroethane, 1-nitropropane, and 2-nitropropane are proposed.

The first involves a reduction of the nitro compound to the corresponding amine, and the identification of the amine as a di-alkyloxamide by reaction with diethyl oxalate, as an N-alkyl-2,4-dinitroaniline by reaction with 2,4-dinitrochlorobenzene, or as a alkyl-phenylthiourea by reaction with phenyl isothiocyanate.

The other method consists of a reaction between the sodium salt of the nitroparaffin and a diazonium salt from either aniline, p-nitroaniline, p-toluidine, or β-naphthylamine to give a nitro-aldehydephenylhydrazone.

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AUTOBIOGRAPHY

I, John Willard Hutcheson, was born in Rothville, Missouri, July 18, 1917. My elementary and high school education were received in the Brookfield Public Schools at Brookfield, Missouri.

My undergraduate work was done at Central College, Fayette, Missouri, where I received the degree of Bachelor of Arts in May, 1939. In the fall of 1939 I entered Oklahoma Agricultural and Mechanical College as a graduate assistant in the Chemistry Department. Here, during the past two years, I have pursued studies leading toward the degree of Master of Science in Chemistry.

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