THE NITRATION OF PARAFFIN HYDROCARBONS.

A Thesis

Submitted to the Faculty of Graduate Studies and Research of McGill University in Partial Fulfillment of the Requirements for the Degree of Master of Science.

by

Robert W. Schiessler

Montreal, Canada May, 1941

The author gratefully acknowledges the assistance and direction of Dr. P. G. Stevens, under whom this research was completed, and the helpful guidance of Dr. J. H. Ross in the writing of this thesis.

Table of Contents

INTRODUCTION

Although nitration is one of the oldest reactions employed in organic chemistry, relatively little is known about its mechanism. Virtually no work has appeared on the mechanism of direct nitration of alkanes, and even though a great number of papers which deal with the nitration of aromatic compounds and alkenes have been published, the nature of these reactions is still obscure. The following review will be confined to the nitration of paraffin hydrocarbons, and will refer to other reactions only when it is necessary to elucidate.

Saturated paraffin hydrocarbons have come to be regarded as extremely stable compounds which are not easily attacked by chemical reagents, and although in some measure this is true, it is probable that the emphasis is unjustified. The fundamental difference between saturated and unsaturated hydrocarbons is that the former yield only substitution products whereas the latter may give both addition and substitution products, e.g.:

$$CH_3.CH_3 + Cl_2 \longrightarrow CH_3.CH_2.Cl + HCl$$

$$CH_2{=}CH_2 + 2Cl_2 \longrightarrow CH_2Cl.CH_2Cl \longrightarrow CH_2.Cl.CHCl_2 + HCl$$

The gaseous members of the series are the most resistant to chemical action, but this attribute decreases markedly with increase in molecular weight.

The most stable members are those containing a quaternary carbon atom, in which one carbon atom is attached directly to four other carbon atoms, whereas the most reactive molecules contain a tertiary carbon atom. (i.e., a carbon linked directly to three other carbon atoms.) This property of tertiary hydrocarbons probably accounts for the fact that they are easily nitrated by dilute nitric acid, giving a fair yield of tertiary nitroparaffins together with some primary and secondary.

When these tertiary nitro compounds are subjected to the conditions of nitration usually employed in preparing the primary nitroparaffins (conc. nitric acid-sulfuric acid mixture), a large proportion of the tertiary compound is oxidized and thus destroyed. This reasoning is in accord with Konawalow's (1) conclusions, which are as follows:

1. Tertiary hydrogen atoms are easily replaced by nitro groups by direct nitration.

2. Primary hydrogen atoms are the most difficult to replace.

3. Nitration precedes oxidation.

4. Oxidation occurs on the carbon atom to which the nitro group is attached.

5. The rate of nitration and the rate of oxidation increases with increase in the concentration of the nitric acid.

As it was apparent that nitration of saturated hydrocarbons involved the substitution of a nitro group for a hydrogen atom, it was decided to conduct this research in an attempt to clarify the mechanism of this interchange. With this object in mind, the nitration of a representative optically active tertiary hydrocarbon was tried, in order to determine whether the product of replacement of the tertiary hydrogen by a nitro group would be optically active.

HISTORICAL REVIEW

Nitration of Paraffinic Hydrocarbons.

Nitroparaffins were first produced in 1872 by Victor Meyer (2), who prepared them by the reaction which bears his name:

$$R.I + AgNO_2 \longrightarrow R.NO_2 + RONO + AgI$$

The mixture of alkyl nitrites and nitroparaffins was easily separated, since the nitrite esters boiled about one hundred degrees (C.) lower than the corresponding nitro compounds. In 1880 Beilstein and Kurbatow (3) succeeded in obtaining mono-nitrocyclohexane by direct nitration of a petroleum fraction, however, the nitration of paraffin hydrocarbons was first studied in the years between 1892 and 1907.

Konawalow (4) in 1894 reported a fair yield of 2-nitrooctane from the nitration of n-octane in a sealed tube at 130° C. using dilute nitric acid (sp. gr. = 1.075), whereas Worstall (5) in 1898 obtained primary mono- and di-nitrooctanes using a boiling mixture of concentrated nitric and concentrated sulfuric acid for several days, and in the same publication reports a 60 per cent yield of nitrated product by several days boiling of n-hexane with concentrated nitric acid (sp. gr. 1.42) Nitro compounds have also been produced by reacting paraffins

with fuming nitric acid at 10° C. by Markownikow (6), but under these conditions oxidation seemed to be greatly facilitated. Konawalow (4;7) prepared mono- and di-nitro compounds from a variety of saturated hydrocarbons, and demonstrated that his method (sealed tube; dilute nitric acid; temperature over 100° C.) was widely applicable. From his results one may conclude that the tertiary hydrocarbons (R_3C-H) are most easily attacked, giving fair yields of tertiary nitroparaffins. When saturated hydrocarbons are nitrated, the nitro group tends to attach itself to a tertiary carbon atom; if such an atom is not present, a secondary rather than a primary carbon atom is most amenable to substitution by the entering nitro group. This fact is strikingly shown in the nitration (8) of diisobutyl (2,5-dimethylhexane), which yields a nitrated product consisting of 83 per cent of the 2-nitro (tertiary) compound and 17 per cent of the 1-nitro and 3-nitro derivatives.

$$CH_3.\underset{\displaystyle CH_3}{\underset{|}{CH}}.CH_2.CH_2.\underset{\displaystyle CH_3}{\underset{|}{CH}}.\ CH_3 \longrightarrow CH_3.\underset{\displaystyle NO_2}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}.CH_2.CH_2.\underset{\displaystyle CH_3}{\underset{|}{CH}}.CH_3$$

The most difficult of all to nitrate are the quaternary paraffins of the type $R_4.C$, and use of this property has actually been made to separate these compounds from the other paraffins (9).

In 1898 Francis and Young (10) drew up the following postulates which express the order of reactivity of

hydrocarbons with fuming nitric acid:

1. Aromatic hydrocarbons and the alkyl derivatives of the cycloparaffins react at ordinary temperatures.

2. Tertiary paraffins (R_3CH) react when heated on the water bath.

3. Cycloparaffins and straight chain or normal paraffins compounds are slowly attacked when heated on the water bath.

Direct nitration of paraffins containing less than five carbon atoms has recently (1936) been accomplished by Hass (11) by employing a vapor phase reaction. The method is quite simple and consists of passing the gaseous hydrocarbon through boiling nitric acid, then conducting the gaseous mixture of paraffin and nitric acid through a spiral glass reaction tube immersed in a KNO_3-$NaNO_3$ bath heated to 350°-410° C., finally condensing the mixture of nitroparaffins formed by passing the exit gases through a series of condensers. They report yields up to 40 per cent nitrated product per pass when using butanes. It is important to note that in all the nitrations carried out by these workers, the temperature was well above the critical temperature of the reacting hydrocarbon. Under these rather drastic conditions, the resulting product is not solely a mixture of isomeric nitroparaffins of the same carbon content as the starting material, but is made up of all the nitro compounds

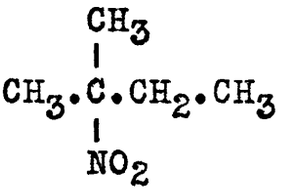
which could be obtained from the theretically possible free radicals that might be formed by less of hydrogen or through carbon-to-carbon fission. The following table lists the free radicals possible from isopentane (2-methylbutane), together with the nitroparaffins which were isolated from the nitration of this substance (12).

Possible Free Radicals	Corresponding Nitroparaffin
$CH_3.CH_2.CH.CH_2-$ | CH_3	$CH_3.CH_2.CH.CH_2.NO_2$ | CH_3
$CH_3.CH.CH_2.CH_2-$ | CH_3	$CH_3.CH.CH_2.CH_2.NO_2$ | CH_3
| $CH_3.CH_2.C.CH_3$ | CH_3	NO_2 | $CH_3.CH_2.C.CH_3$ | CH_3
$CH_3.CH.CH.CH_3$ | | CH_3	$CH_3.CH.CH.CH_3$ | | NO_2CH_3
$CH_3.CH_2-$	$CH_3.CH_2.NO_2$
$CH_3.CH_2.CH-CH_3$ |	$CH_3.CH_2.CH.CH_3$ | NO_2
$CH_3.CH.CH_2-$ | CH_3	$CH_3.CH.CH_2-NO_2$ | CH_3
$CH_3.CH.CH_3$ |	$CH_3.CH.CH_3$ | NO_2
CH_3-	CH_3-NO_2

It was determined that about 50 per cent of the yield from this nitration of isopentane consisted of primary nitro compounds, with the remaining 50 per cent made up of secondary and tertiary derivatives, which were present in about equal proportions. The reaction was carried out at both 380° C. and 420° C., and the average yield of nitroparaffin was about 17.5 per cent. These workers (11) found that the use of catalysts gave poor results: aluminum nitrate was ineffective: silica gel and platinum were found to promote oxidation. When air or oxygen was introduced, oxidation was increased, without apparently affecting nitration. Super atmospheric pressure increased both the yield and reaction rate; e.g., at three atmospheres the yield was 15 per cent greater.

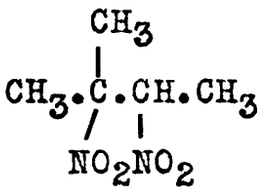
Poni and Costachescu (13) studied the effect of acid concentration in the nitration of isopentane and discovered that nitric acid of specific gravity 1.075 to 1.14 would only nitrate this hydrocarbon with difficulty below 140° C., whereas acid of specific gravity 1.38 to 1.42 would attack the paraffin at 60° C., yielding oxidation and nitration products. They obtained their best yields, consisting of mono-, di-, and tri-nitro derivatives, using 1.42 acid at 60° C., with a molar ratio of 1.5 parts acid to 1.0 part of hydrocarbon. With the dilute acid at about 135° C. in sealed tubes, these

authors report the tertiary nitro compound,

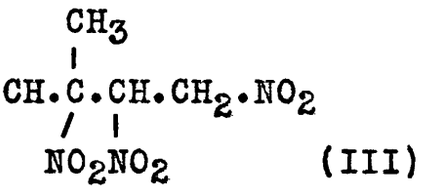


(I)

Whereas with the concentrated acid at 60° C. they obtained (I),(II) and (III):

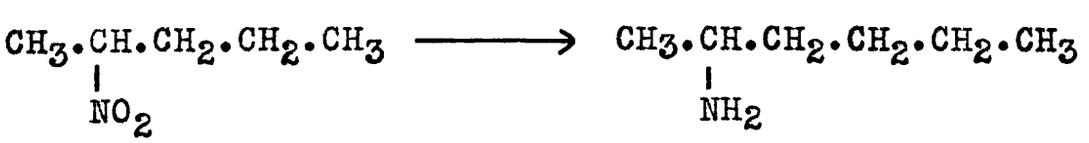


(II)



(III)

In 1894 Konawalow (14) reported that nitration of n-hexane in a sealed tube at 115°-120° C. using nitric acid of specific gravity 1.155 gave only a small yield of nitro-paraffin, however, at 140° C. with acid of specific gravity 1.075, he obtained a 60 per cent yield of 2-nitrohexane, this structure being proved through reduction with zinc and acetic acid, which gave 2-amino-hexane and 2-hexanone.

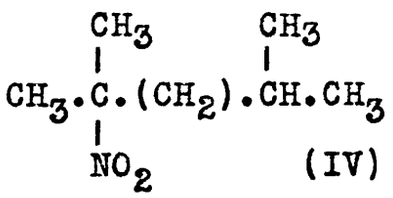


In contrast to this, when n-hexane is boiled for three or four days with nitric acid of specific gravity 1.42 to 1.52 (15), a 60 per cent yield of nitrated product,

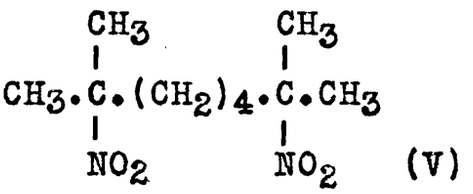
principally composed of 1-nitrohexane, is obtained. Oddly enough, the lower members of the series are water-white liquids, but 1-nitrohexane is reported to be a light yellow.

$$CH_3.CH_2.CH_2.CH_2.CH_2.CH_3 \longrightarrow CH_3.CH_2.CH_2.CH_2.CH_2.CH_2.NO_2$$

When 2,7-dimethyloctane (diisoamyl) is nitrated (16) by Konawalow's method, the product consists mainly of 2-nitro-2,7-dimethyloctane (IV), together with some 2,7-dinitro-2,7-dimethyloctane (V):

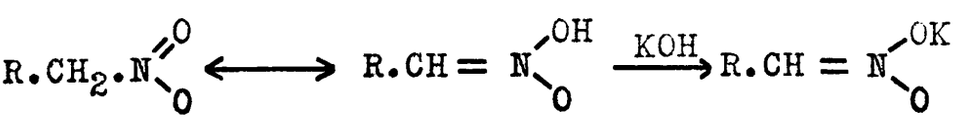


(IV)

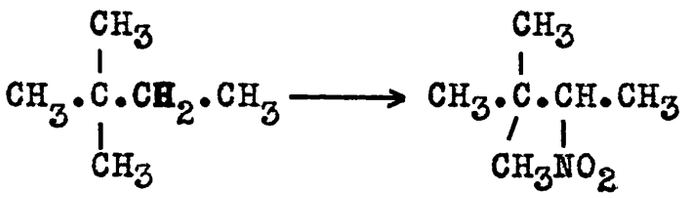


(V)

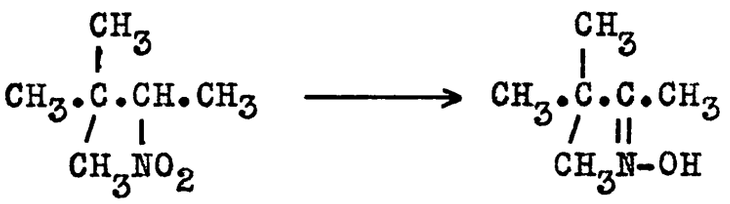
This paraffin, like most saturated hydrocarbons containing two tertiary-carbon atoms, is attacked readily by nitric acid at 20° C. Isomeric primary or secondary nitroparaffins which might be formed are easily separated from the tertiary compounds by repeated extraction with alcoholic potassium hydroxide solution (16), the water-soluble potassium salts of the aci-nitro tautomers being formed. Since there is no hydrogen on the carbon atom to which the nitro group is linked, the tertiary nitroparaffins are incapable of yielding the aci-nitro form, and are therefore insoluble in alkali.



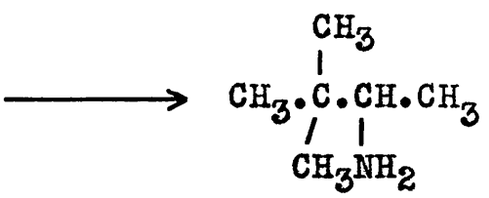
2,2-dimethyl butane (neohexane), one of the quaternary paraffins, can be nitrated (17) with difficulty to 2,2-dimethyl-3-nitrobutane



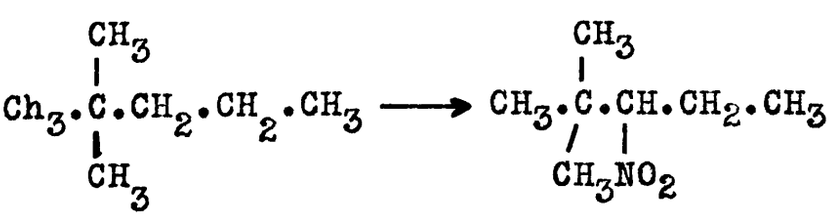
The structure of the product was proved by alkaline reduction with stannous chloride, which yielded the oxime of pinacolone:



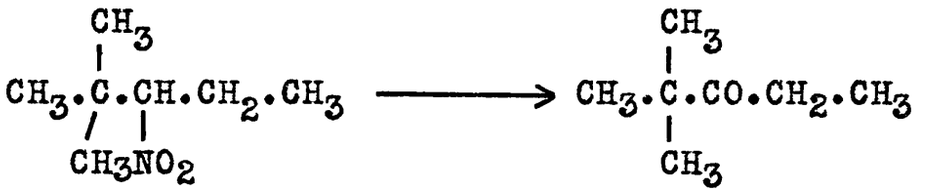
and reduction with tin and hydrochloric acid, which gave the corresponding amine, 2,2-dimethyl-3-aminobutane:



With an analogous compound, 2,2-dimethyl pentane (neoheptane), Markownikow (18) obtained 2,2-dimethyl-3-nitropentane by heating for twenty-seven hours in a sealed tube at 110°-115° C. with nitric acid of specific gravity 1.235.



This structure was proved by hydrolysis of the nitroparaffin with alkaline zinc chloride to the corresponding ketone, 2,2-dimethylpentanone-3:



It is interesting to note that when he employed the conditions (10 hours; sealed tube at 110° C.; acid of sp. gr. 1.075) which are best for nitrating tertiary paraffins, there was no trace of nitro compound formed from this quaternary hydrocarbon.

From these examples it appears to be a general rule that nitration of a quaternary paraffin hydrocarbon (typified by the structure $R_4.C$) takes place in such a manner that the entering nitro group becomes attached to the carbon atom next to the tertiary butyl group $(CH_3)_3C$-, without rearrangement.

In 1905 Konawalow (19) showed that nitration of 3-ethylpentane (triethylmethane) by his procedure, employing dilute nitric acid in a sealed tube at 120° C., results in the formation of a nitrated product consisting of 57 per cent of the tertiary nitro compound, 3-ethyl-3-nitropentane, and 43 per cent primary and secondary nitro compounds.

The nitration of n-heptane has been studied by a number of workers. Konawalow (20) reported the preparation of 2-nitroheptane by heating in a sealed tube to 125° C. with nitric acid of specific gravity 1.075. According to Worstall (21), n-heptane is much more easily nitrated with nitric acid of specific gravity 1.42-1.52 and the boiling hydrocarbon than is n-hexane. The reaction proceeds as follows:

$$CH_3.(CH_2)_5.CH_3 \longrightarrow CH_3.(CH_2)_5.CH_2.NO_2 \longrightarrow$$

$$CH_3.(CH_2)_5.CH(NO_2)_2$$

Haines and Adkins (22), in a study of the nitrations of a variety of hydrocarbons, found that n-heptane was quantitatively nitrated by nitrogen pentoxide at 0° C. The product decomposed when they attempted to distill it at atmospheric pressure.

When n-octane is nitrated by the method of Konawalow (23), employing dilute nitric acid (d=1.075) in a sealed tube at 130° C., a fair yield of the secondary nitroparaffin, 2-nitrooctane, results. Nitration of this hydrocarbon with a mixture of concentrated nitric and concentrated sulfuric acids (24) at the boiling point of the paraffin yields mainly 1-nitrooctane and 1,1-dinitrooctane, whereas with fuming nitric acid oxidation occurs.

Urbanski and Slon (25) have nitrated most of the straight-chain hydrocarbons up to n-decane, employing

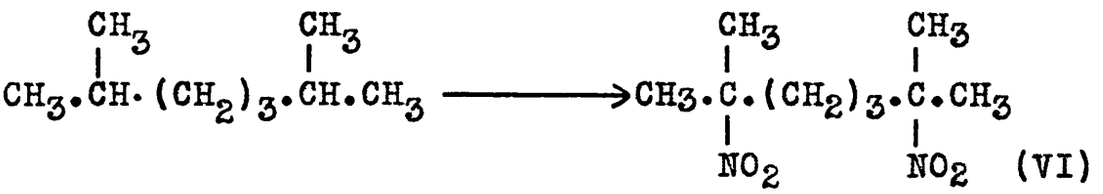
nitrogen tetraoxide in the vapor phase. The method is quite simple: nitrogen tetrooxide gas is bubbled through the boiling hydrocarbon and the mixed vapors conducted through a glass reaction tube maintained at 100°-200° C. The nitration products are condensed after removal of excess nitrogen tetroxide with cold air, and fractionated in vacuo. By this procedure these authors obtained mainly primary nitroparaffins, both mono- and di-nitro, together with some secondary derivatives, all of which were characterized by reduction to the corresponding aldehydes or ketones with zinc and acetic acid. The principal reaction may be represented as follows:

$$2\ CH_3.(CH_2)_x.CH_3 + 4NO_2 \longrightarrow 2CH_3.(CH_2)_x.CH_2.NO_2 + H_2O + N_2O_3$$

They report yields of from 30 to 80 per cent nitrated product, depending on conditions. The ratio of mono- to di-nitroparaffin was usually about 60/40; thus, nitration of n-pentane, n-hexane, n-heptane, n-octane, and n-nonane gave mono-and di-nitro derivatives approximately in these proportions.

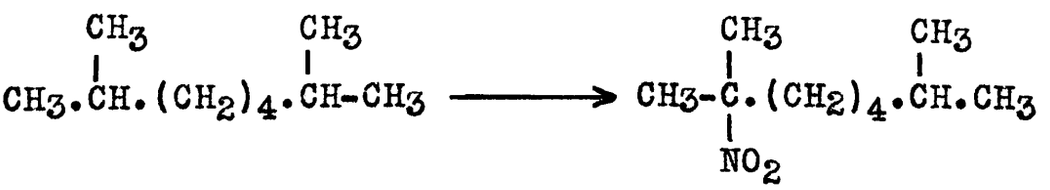
The branched chain isomers of the higher members of the series have been nitrated by several workers, and in every case where a tertiary carbon atom (R_3C-H) was present a good yield of the tertiary nitroparaffin was obtained. The nitration of 2,5-dimethylhexane (diisobutyl)

resulted primarily in the formation of the tertiary 2-nitro-2, 5-dimethylhexane, a yellow oil. Konawalow showed (27) that reaction of 2,6-dimethylheptane with dilute nitric acid (d=1.075) in a sealed tube at 120° C. yields a nitrated product consisting of 60 per cent tertiary nitroparaffin and 40 per cent a mixture of the primary and secondary isomers. When nitric acid of specific gravity 1.11 was used, a fair yield of the tertiary dinitro product, 2,6-dinitro-2,6-dimethylheptane, was found:



(VI)

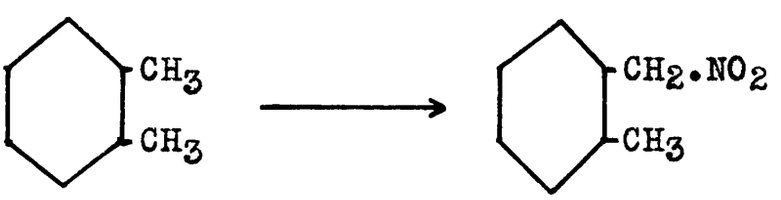
This product (VI) is a white, crystalline solid, melting at 74°-75° C. The same worker (27) studied the nitration of 2,7 dimethyloctane (diisoamyl), an analogous compound. It was demonstrated that when concentrated nitric acid (d=1.38) was used, a great deal of oxidation took place; utilization of progressively weaker acid required longer heating but gave much better results: a better yield of nitroparaffin, less oxidation, fewer polynitro compounds. With acid of specific gravity 1.075 in a sealed tube at 110° C., Konawalow obtained a good yield of 2-nitro-2, 7-dimethyloctane.



In this same nitration study it was discovered that used acid and recovered hydrocarbon react more quickly than does the fresh material. The author reports that use of aluminum nitrate as a catalyst is of value. This salt ($Al(NO_3)_3.9H_2O$) or bismuth nitrate ($Bi(NO_3)_3.5H_2O$) when used as nitrating agents in open vessels yield mainly primary and secondary mono-nitro compounds.

Worstall (28) reports the nitration of nonane, decane, hendecane and dodecane with nitric acid of specific gravity 1.80. He was able to separate the mono- and di-nitro compounds by steam distillation. Nitrononane was a pale yellow oil.

The method of Konawalow is specific for nitrating paraffin hydrocarbons. For example, when o-xylene is heated to 110° C. with dilute nitric acid (d.=1.075), nitration of the aliphatic side-chain takes place with the formation of ortho-tolyl nitromethane, a primary nitro compound (29):



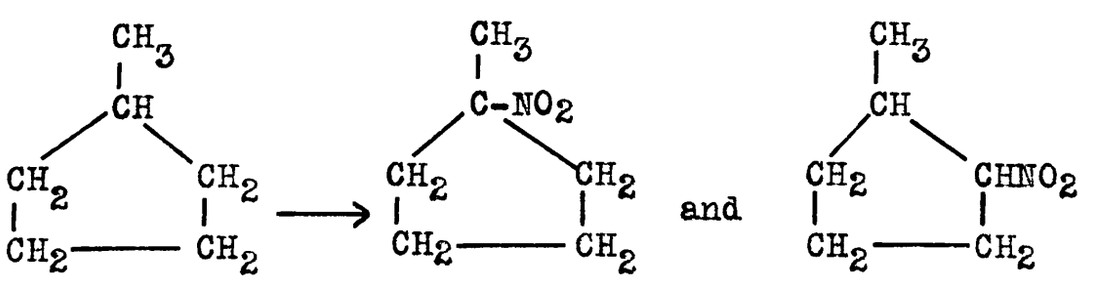
There is no nitration of the aromatic nucleus. Dilution of the nitrating acid with acetic acid gives the same effect.

Nitration of the Cycloparaffins.

The saturated five and six-membered ring hydrocarbons are attacked by nitric acid, yielding oxidation products and nitro compounds. Fuming nitric acid vigorously

oxidizes the cycloparaffins (30) at temperatures above 0° C., whereas with dilute nitric acid at temperatures above 100°.C. nitro compounds are formed. As in the case of the acyclic paraffins, nitration of the alicyclic saturated hydrocarbons proceeds in such a way that the entering nitro group has the greatest tendency to become attached to a tertiary carbon atom, although secondary and primary derivatives are also formed. The alkyl derivatives of cyclopentane are more easily attacked than the corresponding cyclohexane homologues.

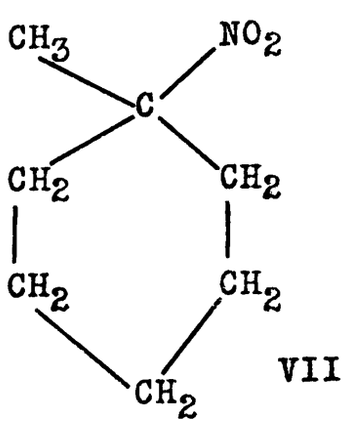
Markownikow (31) reports that methyl cyclopentane is not attacked in the cold by a mixture of concentrated nitric and sulfuric acid, But can be nitrated with dilute nitric acid (d.=1.075) in a sealed tube at 115-20° C. to yield the tertiary 1-nitro-1-methylcyclopentane as the main product, together with some 2-nitro-1-methyl-cyclopentane:



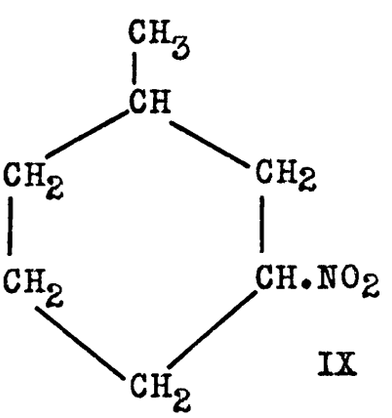
These products, which were also reported by Nametkin (32), can be reduced to the corresponding amino-derivatives with tin and hydrochloric acid.

The nitration of cyclohexane (33) by Konawalow's method yields mono-nitrocyclohexane. In 1910 Nametkin (34) nitrated this hydrocarbon using aluminum nitrate ($Al(NO_3)_3 \cdot 9H_2O$) at 110°-115° C. instead of nitric acid, and obtained as mono-nitrocyclohexane as the chief product, together with cyclohexanone and dinitrocyclohexane. This salt gives the equilibrium concentration of nitric acid at any temperature above its melting point, (90° C.) which of course remains constant as long as any of the salts remains. The weight of the aluminum nitrate used was three times as great as that of the cyclohexane, and a 56 per cent yield of nitrated product was realized, being better than that obtained with dilute nitric acid.

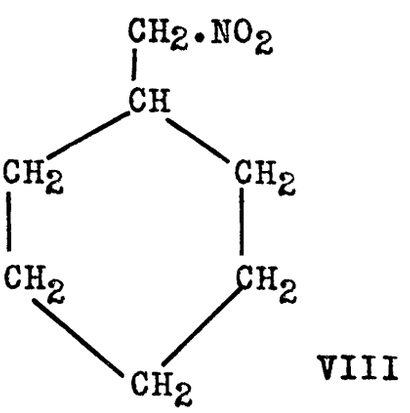
The reaction between methyl cyclohexane and nitric acid was studied by Markownikow (35), who found that fuming nitric acid vigorously oxidized this naphthene, although it was unattacked by mixed acid (conc. HNO_3 - conc. H_2SO_4) up to 80° C. The sealed tube nitration, using nitric acid of specific gravity 1.2, gave a 58 per cent yield of nitrated product, composed of mainly the tertiary (VII) isomer, together with some primary (VIII) and secondary(IX):



VII



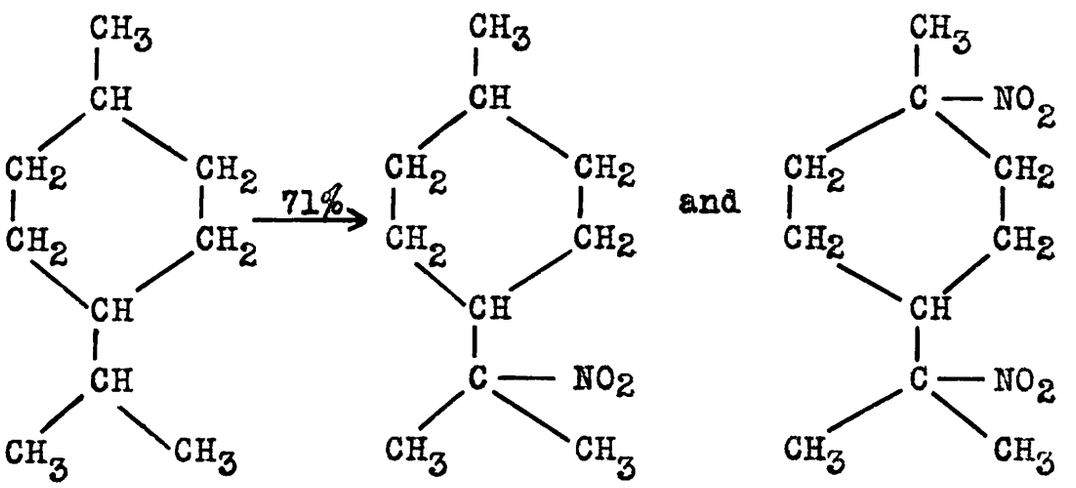
IX



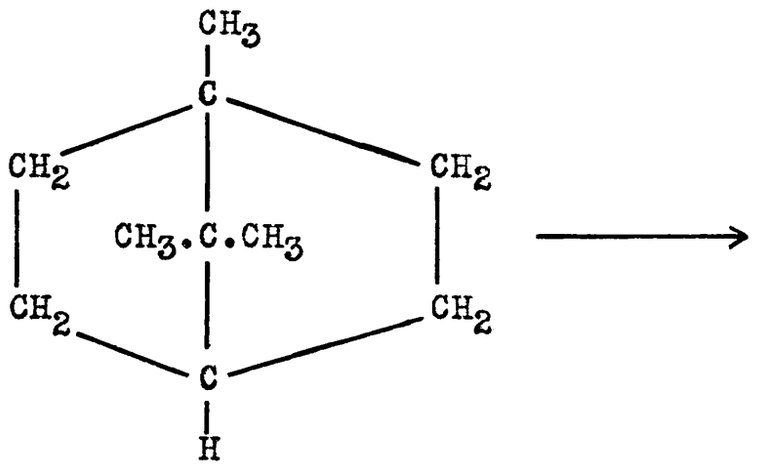
VIII

Nametkin (36) reports the formation of the same products in 72 per cent yield from nitration of methylcyclohexane with aluminum nitrate.

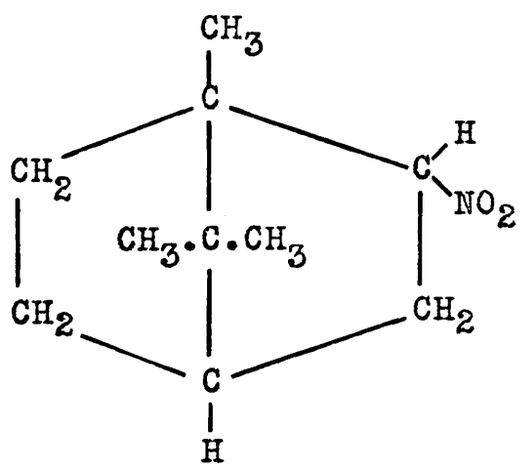
Relatively few of the more highly substituted cycloparaffins have been nitrated. Konawalow and Jebenko (37) reacted p-methane with dilute nitric acid (d.=1.075) in a sealed tube and obtained a nitrated product consisting of 7$ per cent tertiary and 29 per cent secondary nitro compounds.

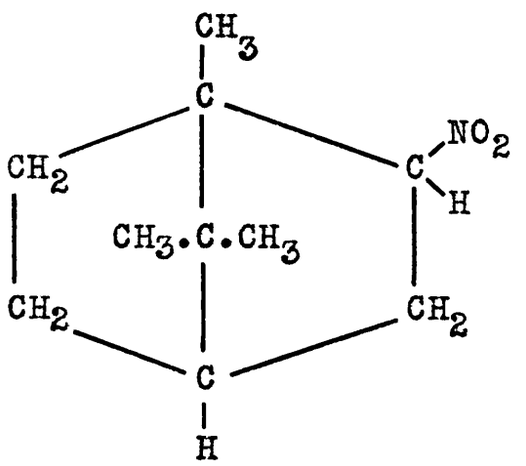


In 1902, Konawalow and Kikina (38) reported the nitration of camphane. This work was carefully repeated in 1915 by Nametkin (39), using dilute nitric acid in a sealed tube at 145-50° C. The nitrated product consisted of two stereoisomeric nitrocamphanes which were separated by fractional crystallization. The reaction may be represented as follows:



camphane





α - nitro camphane

M. pt. = 128°-130° C.

β - nitro camphane

M. pt. = 146°-147° C.

It is significant that none of the tertiary isomer was obtained.

THEORETICAL DISCUSSION

The Mechanism of Nitration of Paraffin Hydrocarbons.

Although a large amount of work has been completed purporting to show the mechanism of the nitration of aromatic hydrocarbons, this reaction is still not clearly defined. The nitration of aliphatic hydrocarbons has not been nearly so thoroughly studied, and the mechanism of this reaction is obscure. This discussion will be confined, for the most part, to nitration of saturated hydrocarbons, and will refer to other reactions only when that resource is necessary for clarity.

Since most nitration reactions employ nitric acid in one of several mixtures, it should prove instructive to review some of the important properties of these reagents. Nitric acid can function both as an oxidizing and nitrating reagent, and these properties are dependent on concentration and temperature, both reactions being accelerated by the presence of nitrogen oxides. From these facts it is evident that nitration will be limited only by ease of oxidation of the substance to be nitrated. In the case of aliphatic compounds, temperature appears to be more important than concentration, the reverse being true in the nitration of aromatic molecules.

Dilute nitric acid exhibits poor nitrating action and strong oxidizing properties toward aromatic compounds,

whereas the oxidation-resistant paraffinic compounds are nitrated with this reagent, tertiary hydrocarbons ($R_3C.H$) being most readily attacked. These facts attain greater significance when it is remembered that the neutral salts of nitric acid show little or no oxidizing action, though the free acid is a strong oxidizing agent. Investigation (40) of absorption spectra in the ultra-violet has disclosed the following facts:

1. The absorption spectra of dilute nitric acid and of its neutral salts are identical.

2. The absorption bands of concentrated nitric acid and of nitrate esters are the same.

3. The absorption spectra found in (1) is different from that found in (2).

4. Nitric acid of medium concentration exhibits both absorption bands.

From these facts it may be deduced that the structure of the nitric acid molecules in dilute and concentrated solutions is not the same. According to Brunetti and Ollano (41), a study of concentrated nitric acid by means of the Raman effect shows that the molecular form $HO.NO_2$ is present. Since gaseous nitric acid exhibits the same absorption band as does the concentrated acid, it is evident that the concentrated form is undissociated. Structures may now be assumed (42) to explain these facts,

(X) explaining the properties of dissociated dilute acid, and (XI) those of the undissociated concentrated form:

$(H)(NO_3)$ $(HO.NO_2)$

X XI

Both of these forms are found in acid of medium concentration, and hence concentrated nitric acid is a rather neutral complex, whereas the dilute material is a true acid. Hantzsch has also shown that the concentrated nitric acid is a mixture of the following forms:

a. Pseudo-acid $HO.NO_2$

b. Nitronium Nitrate $(HO)_3N(NO_3)_2$

c. Hydroxonium Nitrate $(H_3O)(NO_3)$

d. True acid HNO_3

e. Dissociated true acid $(H^+)(NO_3^-)$

As would be expected, the relative concentrations of (d) and (e) vary in the same direction when the concentration is varied, and the ratio of (a) to (d) decreases with decreasing concentration of acid.

From these facts it is immediately evident that the acid concentrations most favorable to nitration of the paraffinic hydrocarbons (d.=1.075 to 1.1; containing 13 to 17 per cent nitric acid) are those which contain true nitric acid in the dissociated and undissociated forms, with little if any pseudo-acid present (32 per cent acid contains only 2 per cent $HO.NO_2$). Therefore one or both of these forms is most likely to be reponsible

for the actual nitration, since nitric acid of specific gravity 1.075 is only 73 per cent dissociated or ionized at 25° C. (43). Usanovich (44) has expressed the view that the nitration of aliphatic compounds is due to the nitrate anion, one of the possibilities which follows directly from the above discussion. This fact was anticipated by the author and an attempt was made to effect the nitration of 3-methylheptane with a solution of barium nitrate at 135° C. without success. Therefore, since neutral salts of nitric acid exhibit little or no oxidizing or nitrating action, and since dilute nitric acid (which, however contains the undissociated true acid) has been shown to be active in both of these functions, it is probable that the nitrating and oxidizing agent present is actually the undissociated true acid, HNO_3.

This arguement is, of course, invalid in the case of nitrations employing concentrated nitric acid, for in these reactions the acid may consist of as much as 100 per cent of the pseudo-acid, $HO.NO_2$, and it is likely therefore, that this form is the true nitrating agent. However, it has been shown in the historical that in the case of progressively more concentrated nitric acid (13) the tendency is toward formation of primary and secondary nitro compounds, whereas dilution of the nitrating reagent appears to effect direction of the entering nitro group toward tertiary carbon atoms,

of the type $R_3.C.H$. It is probable that this effect is due in part to the nature of molecular structure of the actual nitrating reagent and that primary hydrogen atoms are more easily replaced by the pseudo-acid $HO.NO_2$, whereas the tertiary carbon atoms react better with the undissociated true acid molecules, HNO_3. Usanovich (44) has suggested that due to the amphoteric mature of nitric acid (45,46), the nitrating agents in a mixture of concentrated nitric and sulfuric acids are the cations $NO(OH)_2$ and $N(OH)_3$. It may be argued that in nitrations employing dilute nitric acid, the true nitrating agent is the nitrogen tetraxide (NO_2 or N_2O_4) formed from the nitric acid through an initial oxidation of the hydrocarbon. This view is upheld by the work of Urbanski and Slon (47), in which these authors effected the nitration of paraffin hydrocarbons in a vapor phase reaction using nitrogen tetroxide at 100° to 200° C. As has been shown, however, (see pages 13-14 of Historical) this method of nitration results mainly in the formation of primary mono- and di-nitro products, in contrast to Konawalow's dilute-acid, sealed tube method, which yields primarily tertiary and secondary nitro compounds. Further, if NO_2 is the actual nitrating agent operative in the sealed tube reaction, it would be expected that the opening of the tube would release the characteristic red-brown fumes of nitrogen tetroxide. In none of the nitrations carried out in this manner by the author were these gases noticed.

The significance of the formulae assumed for true nitric acid and the pseudo-acid is as follows: in the case of the true acid, HNO_3, the proton or hydrogen nucleus is pictured as being attached or bound electrostatically to the whole nitrate anion (NO_3); for the pseudo-acid ($HO.NO_2$), this hydrogen nucleus is believed to be attached through sharing of two electrons with one of the oxygen atoms, i.e., by means of covalent bonding (48).

One suggestion for the mechanism of nitration (49) is that the substitution involves direct metathesis:

$$R.H + HO.NO_2 \longrightarrow R.NO_2 + HOH$$

This , of course, is the over-all effect, but it fails to explain the electronics involved. McCleary and Degering (50), in attempting to clarify the vapor phase nitration of paraffin hydrocarbons (11), postulate the formation of free radicals. These workers at first held the view that, since nitric acid vapor is completely decomposed at 250° C. into nitrogen dioxide (NO), nitrogen tetroxide (NO_2), water and oxygen, and because the nitrations were carried out at 380° to 420° C., the actual nitration was accomplished by either NO or NO_2. Therefore, they reasoned, since the nitrogen tetroxide molecule contains an odd electron (and therefore is a free radical), collision with a free radical would result in a stable compound. An attempt to prove this, employing tetraethyl lead as a source of free radicals resulted usually in an explosion, which these authors believe due to the form-

ation of ethyl nitrite:

$$C_2H_5\cdot + \cdot NO_2 \longrightarrow C_2H_5{:}\ ONO$$

The authors explain that probably at the rate of passage of the mixed gases, the nitric acid molecules react without decomposition, and thus the following equations would explain the formation of the products obtained:

$$Pb(C_2H_5)_4 \longrightarrow Pb + 4C_2H_5\cdot$$
$$C_2H_5\cdot + HONO_2 \longrightarrow C_2H_5NO_2 + HO\cdot$$
$$C_2H_5\cdot + HO\cdot \longrightarrow C_2H_5OH$$
$$C_2H_5OH + HONO_2 \longrightarrow C_2H_5ONO_2 + H_2O$$

All the olefins which would be expected from the free radicals which could be formed by cleavage of a carbon-hydrogen bond or fission of a carbon-carbon linkage were found in the exit gases from nitration of propane, butane, pentane (51) and isopentane (52). To explain these facts, McCleary and Degering postulate the following mechanism:

$$R{:}H + \text{free radical or oxidizing agent} \longrightarrow R\cdot + ?$$
$$R\cdot + HO{:}NO_2 \longrightarrow R{:}NO_2 + HO\cdot$$
$$R{:}H + HO\cdot \longrightarrow R\cdot + H{:}OH$$

However, although this explanation satisfactorily accounts for all of the products, it is at once evident that its plausibility is dependent on the formation of free radicals

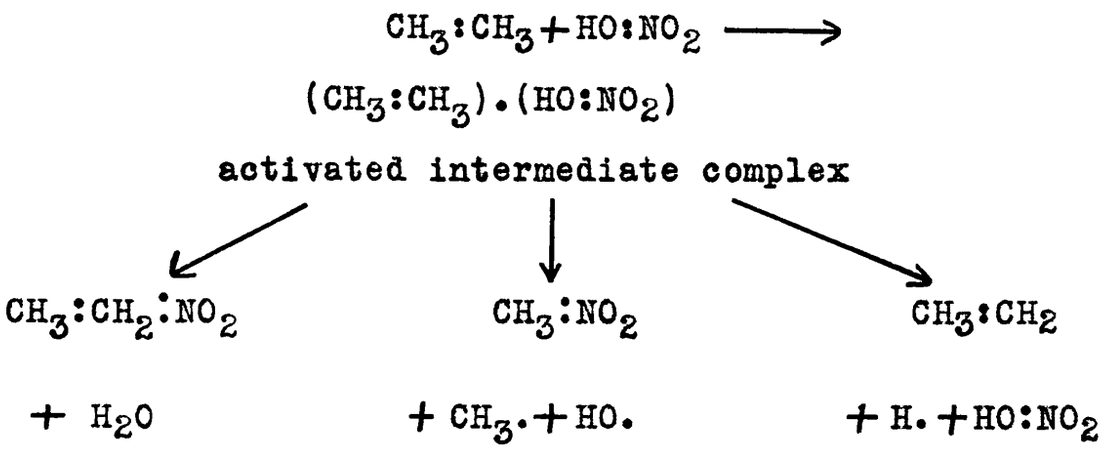
from the hydrocarbons employed. Since these paraffins are more stable than the nitric acid vapors at 400° C., which, as the above authors have pointed out, are totally decomposed at 250° C., it does not seem reasonable that the hydrocarbons should dissociate into free radicals and react with the $HONO_2$ molecules before these can decompose.

In 1939, Ewell (53) proposed intermediate activated complex formation in hydrolysis, chlorination, nitration, sulfonation, amination, and alkylation, basing his arguments on thermodynamic grounds. As an example, in the vapor phase reaction between an alcohol and hydrogen chloride, he postulates the initial formation of an activated molecular complex between the alcohol and hydrogen chloride units, which then could decompose to give either the original materials or the alkyl halide plus water. This may be illustrated as follows:

$$R.OH + HCl \longrightarrow (R.OH).(HCl) \longrightarrow R.Cl + HOH$$

activated intermediate

If this mechanism is now applied to vapor-phase nitration, assuming that the activated complex may decompose in several different ways, all the products obtained can be accounted for without the above discrepancy. For example, the nitration of ethane might then be pictured as below:



At present this appéars to be the most logical mechanism for vapor phase nitration.

The strong electron-release properties of tertiary carbon atoms are well known, and since nitration of tertiary hydrocarbons employing dilute nitric acid (8;10) yields mainly tertiary mono-nitroparaffins, it is probable that this characteristic is very important. When substitution takes place, i.e., when a hydrogen atom is replaced in a saturated hydrocarbon, there are three possible structures which this replaced hydrogen may assume:

(a) It may be released as a proton, or hydrogen atom stripped of its electron. $R_3C{:}H \longrightarrow R_3C{:} + H$

(b) It may be released as a hydrogen atom.

$$R_3C{:}H \longrightarrow R_3C. + H.$$

(c) It may be released as negative hydrogen i.e., a hydrogen atom containing one excess electron and bearing a unit negative charge. $R_3C{:}H \longrightarrow R_3C + H{:}$

If in the nitration reaction, the hydrogen is released as in (a), then it is evident that the original carbon atom

must retain the two covalent electrons, and will have an electronic octet, the normal configuration, although it embraces in this case an unshared pair of electrons. This seems improbable, since as has been explained above, the tendency for a tertiary carbon atom is to release the attached grouping with the covalent electrons.

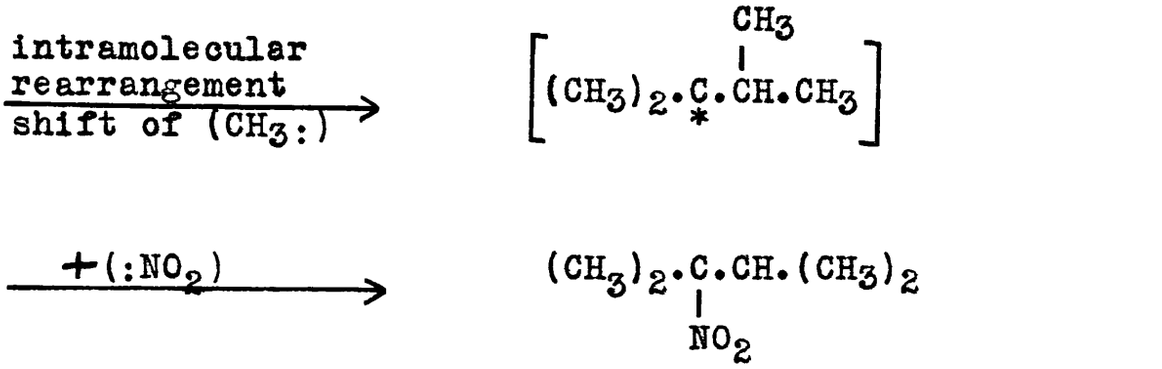
The possibility listed in (c), of the removal of hydrogen as a negative ion, is unlikely in these nitrations for the following reason:

It has been shown (see page 12 of Historical) that the nitration of quaternary paraffins (R_4C) occurs in such a manner that the entering nitro group tends to become attached to a carbon atom in the alpha-position with respect to the quaternary carbon. For example, the nitration of 2,2-dimethylbutane results in the formation of 2,2-dimethyl-3-3 nitrobutane (54):

$$(CH)_3C.CH_2.CH_3 \longrightarrow (CH_3)_3C.\underset{\displaystyle NO_2}{\underset{|}{CH}}.CH_3$$

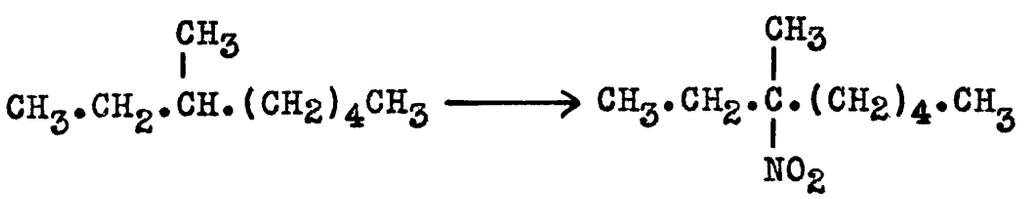
If (c) were correct, then according to Whitmore's (55) mechanism for rearrangement of neopentyl systems ($(CH_3)_3.CH_2$-) the product obtained would consist mainly of 2,3-dimethyl-2-nitrobutane:

$$(CH_3)_2.\underset{\displaystyle CH_3}{\underset{|}{C}}.\overset{\displaystyle H}{\overset{|}{C}}H.CH_3 \xrightarrow{-(H:)} \left[(CH_3)_2.\underset{\displaystyle CH_3}{\underset{|}{C}}.\overset{\displaystyle *}{C}H.CH_3\right]$$



Since none of the rearrangement product is obtained, and since the open-sextet mechanism of rearrangement as illustrated above has been fairly well substaniated, it is improbable that the hydrogen is released as a negative ion, with both the covalent electrons, for then the nitration product should be primarily 2,3-dimethyl-2-nitrobutane.

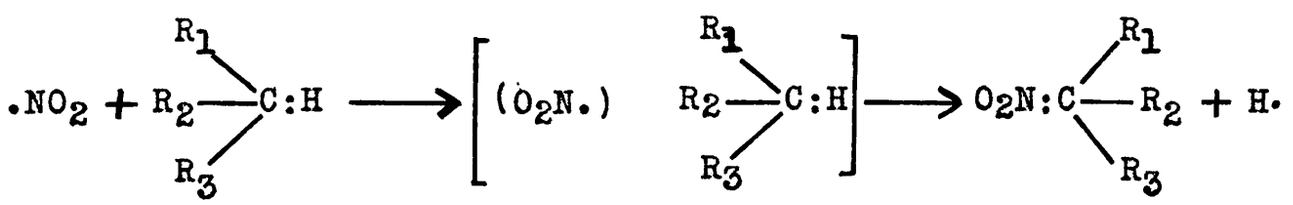
The only remaining possibility (b), in which hydrogen is removed as an atom or free radical, at first seems unlikely since the author obtained levo-3-nitro-3-methyloctane by direct nitration of levo-3-methyloctane employing the sealed-tube dilute-acid method of Konawalow (56).



levorotatory
3-methyloctane

levorotatory
3-nitro-3-methyloctane

This appears improbable because an isolated organic free radical should assume a planar configuration and hence an inactive product would be expected (57). However, an inversion mechanism, similar to that involving ions, need not cause racemization, for the free radical would not be isolated (58,59). By this mechanism, the entering nitro group would approach the face of the tetrahedron opposite the hydrogen atom, and become more or less firmly attached there, forming the activated intermediate complex previously discussed. By a small shift of the nucleus, the asymmetric carbon atom becomes the center of a new inverted tetrahedron, and there is no racemization. This may be represented as follows: ($\cdot NO_2$ is used instead of HNO_3 for the purpose of simplicity)



This mechanism is in accord with the fact that nitration of a bicyclic compound such as camphane (60), which contains a tertiary carbon atom at the bridge-head, yields none of the expected tertiary nitro compound, but instead gives only secondary products. (see pages 19,20 of Historical). As is easily seen, a reaction involving an inversion mechanism is impossible at this tertiary carbon, since the tetrahedral face opposite the attached hydrogen

is protected by the second ring.

Further inductive evidence for the theory of intermediate complex formation lies in the fact that from the formation of an isolated organic free radical from 2,2-dimethylbutane of the type $\left[(CH_3)_3C.\underset{CH_3}{CH}.\right]$ one would expect both cyclic and coupling products, since in the case of free radical formation from 1-chloro-2,2-dimethylpropane (neopentyl chloride) through reaction with metallic sodium, Whitmore reports the products to be 2,2-dimethylpropane (neopentane), 2,2,5,5-tetramethyl-hexane (dineopentane), and 1,1-dimethyl cyclopropane (61), thus:

$$CH_3.\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}.CH_2.Cl \longrightarrow CH_3.\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}.(CH_2)_2.\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}.CH_3 + CH_3.\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}.CH_3$$

13% 36%

$$+ \quad \begin{array}{c} CH_2 \\ / \quad \backslash \\ CH_2 \text{——} C(CH_3)_2 \end{array}$$

25%

Conclusions.

From the forgoing deductions it is concluded that nitration of paraffin hydrocarbons by means of dilute nitric acid most probably proceeds in such a manner that the nitration is accomplished by undissociated true nitric acid (HNO_3) through the medium of an activated intermediate complex between the molecules of acid and saturated hydro-

carbon. This intermediate is formed by attachment of the HNO_3 to the "face-centered bond", the tetrahedral face of the carbon atom opposite the hydrogen to be replaced, and its decomposition is marked by the formation of hydrogen atom and an attached organic "free" radical. At the time of release of the hydrogen atom, the HNO_3 portion of the complex gives up an (HO.) fragment, which probably combines with the hydrogen atom, forming water, and the hydrocarbon residue of the complex undergoes inversion with the formation of a stable nitroparaffin. Thus it is possible for nitration to occur on the asymmetric carbon atom of an optically active tertiary hydrocarbon without racemization, resulting in the formation of an optically active tertiary nitroparaffin (62).

EXPERIMENTAL

1. Preparation of 3-Nitro-3-Methylheptane.

a. Preparation of 3-Methyl-Heptanol-3 (63)

$$CH_3.CO.CH_2.CH_3 + CH_3.CH_2.CH_2.CH_2.MgBr \longrightarrow$$

$$CH_3.CH_2.\underset{\displaystyle OH}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}.CH_2.CH_2.CH_2.CH_3$$

A mixture of 125 gms. (5.1 moles) of magnesium turnings and 750 cc. of anhydrous diethyl ether was placed in a five liter round-bottomed flask equipped with a trident holding a mercury-seal stirrer, a water-cooled Friedrich condenser and a 500 cc. dropping funnel. Stirring was begun and a solution of 685 gms. (5.0 moles) of n-butyl bromide (redistilled; b. pt. 99°-100° C. at 760 mm.) in 800 cc. of anhydrous diethyl ether was added over a period of 2½ hours at such a rate to maintain a vigorous reflux. It was found necessary to keep the flask immersed in an ice-water bath to prevent flooding of the condenser, the solution turning black almost immediately.

The reaction mixture was allowed to stand for twelve hours after reaction was complete, when a solution of 350 gms. (4.9 moles) of redistilled (b. pt. 79-80° C.

at 760 mm.; obtained from Eastman Kodak Co.) methyl ethyl ketone in 250 cc. of anhydrous diethyl ether was added slowly over a period of three hours to the stirred reaction mixture, which was cooled in an ice-water bath. Stirring was continued for an hour after addition was complete, and the reaction product decomposed on ice, dissolving the precipitated magnesium hydroxide by addition of dilute sulfuric acid. The ethereal layer was separated and combined with the ether extracts of the aqueous layer and this solution dried over-night with anhydrous potassium carbonate, filtered, and the ether distilled off. The residue was then transferred to a two-liter round-bottomed flask attached to fractionating column RWS, and the product fractionated under reduced pressure. 450 gms. of 3-methyl heptanol-3 were obtained.

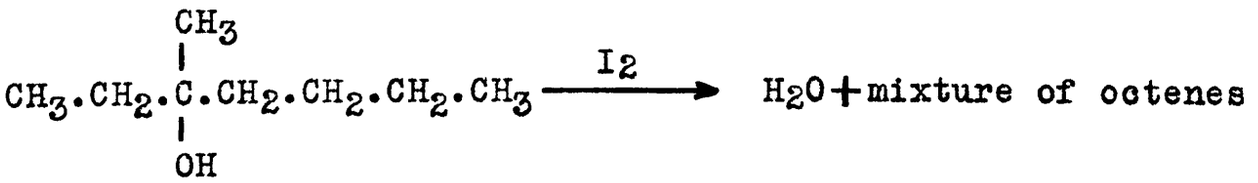
Yield----------450 gms. or 70%

B. pt.----------64°-5° C. at 16 mm.

n_D^{19}----------1.4280

n_D^{25}----------1.4269

b. Dehydration of 3-Methyl Heptanol-3



In a 500 cc. round-bottomed flask was placed a mixture of 390 gms. (3.0 moles) of 3-methyl heptanol-3 (see p. 35,36.) and 0.2 gms. of iodine, the flask then being attached to column RWS and placed in an electrically heated air bath. A mixture of octenes and water was collected at 90°-110° C. over a period of 32 hours, the iodine being renewed three times. The mixture of isomeric octenes was separated from the aqueous, washed with dilute sodium carbonate solution, and dried with anhydrous potassium carbonate. The product was then filtered, transferred to a 500 cc. round-bottom flask attached to column RWS and fractionated at atmospheric pressure.

Yield----------251 gms. or 75%

B. pt.----------120°-123° C. at 762 mm.

c. Preparation of 3-Methylheptane (63,64).

$$\text{mixture of octenes} \xrightarrow[H_2]{Pt.} CH_3.CH_2.\overset{\displaystyle CH_3}{\overset{|}{C}}H.CH_2.CH_2.CH_2.CH_3$$

The mixture of isomeric octenes obtained as on page 36,37 was hydrogenated catalytically in a Burgess-Parr hydrogenation apparatus, using Adams-Voorhees platinum oxide catalyst and glacial acetic acid as hydrogen acceptor at from 2 to 3 atmospheres hydrogen pressure, employing an electrically-heated hydrogenation bottle devised by the author. The 251 gms. (2.25 moles) of octenes was reduced, in 0.5 mole portions employing the following procedure,

which was found to be most effective:

The empty hydrogenation bottle was heated to 80° C., a mixture of 0.5 moles (56 gms.) of octenes and 0.5 gms. of freshly prepared platinum oxide catalyst introduced, the bottle then being swept with hydrogen gas, and the catalyst reduced to colloidal platinum (10 to 15 minutes). The bottle was then opened and 10 cc. of glacial acetic acid added, flushing repeated, and reduction started with pressure initially at 3 atmospheres, it never being allowed to decrease more than 10 pounds. The reaction was exothermic, and the temperature would rise to 90° C., finally returning to 80° C. When this method was employed, absorption was always complete within 40 minutes. The heating and shaking was then discontinued, the bottle allowed to cool, pressure released, and the mixture filtered by decantation. The hydrogenated product was then transferred to a 500 cc. separatory funnel and treated with a solution of potassium carbonate to remove the acetic acid, after which it was shaken for at least 30 minutes with a strong aqueous solution of potassium permanganate to remove any residual olefins, decomposing the excess $KMnO_4$ and precipitate of MnO_2 with a solution of sodium bisulfite. The hydrocarbon was then washed twice with water and dried over anhydrous potassium carbonate.

In this manner all of the prepared olefin was hydrogenated, and the products combined and fractionated

from metallic sodium through column RWS at atmospheric pressure (765 mm.), collecting 180 gms. (1.6 moles) of 3-methylheptane.

Yield----------180 gms. or 70%

B. pt.----------119.0°-119.3° C. at 765 mm.

n_D^{25}----------1.3982

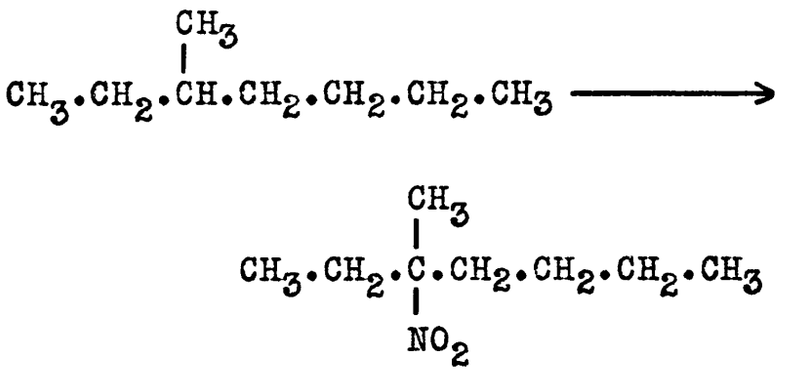
d. Nitration of 3-Methylheptane - General Technique Employed in Nitrations.

In every case where Konawalow's method (27) was used, the following procedure was employed:

A mixture of 5 gms. (0.044 moles) of hydrocarbon and 60 cc. of nitric acid (d. 1.075) was placed in a 50-60 cm. heavy walled pyrex bomb tube, which was then sealed and inserted in a rheostat-controlled electrically-heated bomb furnace, constructed in such a way that constant rocking motion was imparted by an electric motor. The mixture was allowed to react for 12 hours, after which heating was discontinued, the furnace allowed to cool, and the bomb opened by spot-heating with an oxygen hand-torch. The pressure developed within the tube served to blow a small hole through the softened glass, releasing the pressure. The tube end was then drawn out in an oxygen flame, broken off, and the product removed with a long micro-pipette. The originally colorless hydrocarbon layer was then light yellow, and was extracted twice with water, and was then dried over anhydrous sodium sulfate, filtered, and

fractionated under reduced pressure through column BJS.

It was discovered through trial and error that the best yield of tertiary nitroparaffin was obtained when the temperature of the bomb furnace was maintained at 130°-135° C. Practically no nitration product was found at 110° C. Usually three nitrations were run, and the products combined prior to purification. A representative case would be as follows:



From 15 gms. (0.13 moles) of 3-methylheptane (see p. 37,38), after nitration and purification as above, was obtained 5.6 gms. (0.04 moles) of pure 3-nitro-3-methylheptane.

Yield----------5.6 gms. or 31%

B. pt.----------88°-89° C. at 13 mm.

n_D^{25}----------1.4320

D_o^{25}----------0.9361

Nitrogen (Dumas)----------8.6%, 8.9% (found)

8.8% (calculated)

Several open-vessel solvent nitrations employing glacial acetic acid as a diluent in place of water for the

nitric acid, both with and without aluminum nitrate, were tried, with poor results. The best yield obtained was 0.9 gms. of the nitroparaffin from 10 gms. of saturated hydrocarbon, with recovery of 7.5 gms. of the starting material. This method seemed to increase the amount of oxidation greatly, since volumes of brown nitrogen tetroxide fumes were evolved; the temperature was maintained at 105°-110° C. The presence of the salt ($Al(NO_3)_3 \cdot 9H_2O$) was found to favor oxidation.

2. Preparation of dextro-3-Nitro-3-Methylheptane.

(a.) Preparation of dextro-3-Methylheptane.

$$CH_3.CH_2.\underset{\text{dextro}}{\overset{\overset{CH_3}{|}}{CH}}.CH_2.CH_2.CH_2.CH_2.Br \xrightarrow[1/1\ HCl]{\text{zinc amalgam}} CH_3.CH_2.\underset{\text{dextro}}{\overset{\overset{CH_3}{|}}{CH}}.CH_2.CH_2.CH_2.CH_3$$

Preparation of amalgam: In a 250 cc. Erlenmeyer flask was placed a mixture of 90 gms. (1.25 moles) of zinc dust and 90 cc. of a 5 per cent solution of mercuric chloride, the flask then being heated for one hour on the steam cone with frequent shaking. The zinc amalgam was then collected on a Buchner funnel and washed thoroughly with cold distilled water.

Reduction: A mixture of 100 gms. of zinc amalgam (1.3 moles), 50 cc. of 1/1 hydrochloric acid, and 8.5 gms. (0.042 moles) of dextro-3-methyl-7-bromoheptane (obtained from Dr. P. G. Stevens; refractionated, collecting at 75°-76°C. at 13 mm; $(M)_D^{24}$ 4.7° C., about 1/3 resolved) was placed in a 200 cc. round-bottom flask attached to a Friedrich reflux condenser, and refluxing begun. At the end of each hour 10 cc. of concentrated hydrochloric acid were added, until a total of 75 cc. had been used. Refluxing was continued for 14 hours, the mixture cooled and the liquid decanted into a separatory funnel, extracting the residual metal twice with 25 cc. portions of ether, this being then transferred to the separatory funnel together with an additional 25 cc., and the aqueous layer extracted and discarded. The ethereal solution was then washed with dilute potassium carbonate solution to free it of acid, the layers separated, and the ether dried over anhydrous sodium sulfate.

The ethereal solution was decanted through a filter paper into 125 cc. flask attached to column BJS, and the ether fractionated off; the flask was then changed to a 25 cc. size, and the residual liquid fractionated at atmospheric pressure, collecting 2.8 cc. of 3-methylheptane at 118°-119° C.

Yield----------2.0 gms. or 43%

B. pt.----------118°-119° C. at 755 mm.

D_4^{20}----------0.7095

$(\alpha)_D^{24}$----------+2.54° (homogeneous)

$(M)_D^{24}$----------+2.90°

(b) Nitration of dextro-3-Methylheptane.

The 2.7 cc. of dextro-rotatory-3-methylheptane prepared as on pages 41 and 42, was diluted with 8.1 cc. of dl-3-methylheptane (p. 37,38), giving 7.6 gms. of optically active hydrocarbon.

$(\alpha)_D^{24}$----------+0.56° (homogeneous)

$(M)_D^{24}$----------+0.64°

This paraffin was then nitrated in two portions as described on pages 39-40, maintaining the temperature at 130° C., with the following variations: The nitrated hydrocarbon layer was extracted five times with alcoholic potassium hydroxide solution, to ensure freedom from primary or secondary isomers, dried over anhydrous potassium carbonate, and fractionated through column BJS, collecting one cc. of product at 82°-83° C. at 9 mm.

Yield----------0.94 gms.

B. pt.----------82°-83° C. at 9mm.

n_D^{25}----------1.4328

$(\alpha)_D^{24}$----------+0.10° (homogeneous)

This dextro-rotatory tertiary nitroparaffin was then diluted with 7 cc. of inactive 3-methylheptane, extracted twice with 30 cc. of aqueous-alcoholic potassium hydroxide solution, dried, and re-fractionated through column BJS:

Yield----------0.68 gms.

B. pt.----------82°-83° C. at 9 mm.

$(\alpha)_D^{25}$----------+0.10° (homogeneous)

Since there was no apparent change in rotation after this further prification, it was decided that an optically active tertiary nitro hydrocarbon, dextro-3-nitro-methylheptane, had been obtained by direct nitration of dextro-3-methylheptane. To check this result, which showed that nitration occurred <u>without</u> racemization, another optically-active tertiary hydrocarbon, levo-3-methyloctane was prepared and nitrated, as is described in the following procedures.

3. <u>Preparation of 3-Nitro-3-Methyloctane.</u>

(a) <u>Preparation and Dehydration of 3-Methyloctanol-3.</u>

$$CH_3.CO.(CH_2)_4.CH_3 + CH_3.CH_2.MgBr \longrightarrow$$

$$CH_3.CH_2.\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}.(CH_2)_4.CH_3 \xrightarrow{I_2} \text{mixture of nonenes} + H_2O$$

In a three-liter three necked flask equipped with a mercury-seal stirrer, a reflux condenser, and a 250 cc.

dropping funnel was placed a mixture of 82 gms. (3.4 moles) of magnesium turnings and 450 cc. of anhydrous diethyl ether. Stirring was begun and a solution of 350 gms. (3.2 moles) of ethyl bromide in 500 cc. of anhydrous ether was added slowly through the dropping funnel, the solution turning black almost immediately; the addition was complete in three hours, after which the ice-water bath was removed and stirring continued for one-half hour.

A solution of 342 gms. (3.0 moles) of methyl n-amyl ketone or n-heptanone-2 (refractionated; b. pt. = 150°-151° C. at 762 mm.; obtained from Eastman Kodak Co.) in 150 cc. of anhydrous ether was then added dropwise with stirring, the flask being immersed in an ice-water bath. The addition was complete in 2½ hours, stirring being continued for ½ hour with the ice-bath removed. The reaction product was decomposed on ice, the magnesium hydroxide dissolved with dilute sulfuric acid, and the ethereal layer separated and dried over anhydrous potassium carbonate. The ether was removed by fractionating through a stripping column and the residue of carbinol transferred to a one-liter round-bottom flask attached to column RWS and 0.2 gms. of iodine added. The mixture of water and nonenes was collected between 80°-100° C. over a period of 24 hours, renewing the iodine five times. The water layer was discarded, and the mixture of nonenes dried over anhydrous potassium carbonate, filtered, transferred to a one liter

flask attached to column RWS and fractionated from metallic sodium at atmospheric pressure.

Yield----------339 gms. or 90%

B. pt.----------144°-146° C. at 762 mm.

(b) Preparation of 3-Methyloctane (65).

$$\text{mixture of nonenes} \xrightarrow[H_2]{\text{Pt catalyst}} CH_3.CH_2.\underset{\displaystyle CH_3}{\underset{|}{CH}}.(CH_2)_4.CH_3$$

The procedure used, employing catalytic hydrogenation at 2-3 atmospheres is the same as that given under preparation of 3-methylheptane, pages 37-38, with the one exception that the hydrogenation bottle was not externally heated.

In this manner 339 gms. (2.7 moles) of the nonene mixture prepared as on pages 44-45 was hydrogenated, purified as for 3-methylheptane (p.37-38), and dried over anhydrous potassium carbonate. This product was then filtered and fractionated through column RWS at atmospheric pressure, collecting 3-methyloctane at 144°-145° C. at 762 mm.

Yield----------339 gms. or 98%

B. pt----------144°-145° C. at 762 mm.

n_D^{25}----------1.4040

(c) Nitration of 3-Methyloctane.

$$CH_3.CH_2.\underset{\displaystyle CH_3}{\underset{|}{CH}}.(CH_2)_4.CH_3 \longrightarrow CH_3.CH_2.\underset{\displaystyle NO_2}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}.(CH_2)_4.CH_3$$

The procedure employed in these nitrations was identical with that used in nitrating 3-methylheptane, for which refer to pages 39-40.

A representative case would be as follows: From 10 gms. (0.077 moles) of 3-methyloctane (see page 46) after nitration and purification as described on pages 39-40, was obtained 2.2 gms. of fractionated product, 3-nitro-3-methyloctane:

Yield----------2.2 gms. or 17%

B. pt.----------108°-109° at 17 mm.

n_D^{25}----------1.4342

nitrogen (Dumas) ----------8.2% (found)

8.1% (calculated)

4. Preparation of levo-3-Nitro-3-Methyloctane.

(a) Resolution of 2-n-Amylbutyric Acid (2-Methyl-n-Octanoic Acid)(66).

$$dl\text{-}CH_3.(CH_2)_4.\underset{\displaystyle CH_3}{\underset{|}{CH}}.CH_2.CO_2H + \text{quinine} \longrightarrow$$

d-acid.quinine + l-acid.quinine

partially separate by fractional crystallization and decompose.

In 900 cc. of hot acetone was dissolved 200 gms. (1.26 moles) of dl-2-n-amylbutyric acid (redistilled; b. pt. 133°-134° C. at 13 mm; n_D^{25} 1.4290; obtained from Dr. P. G. Stevens) and 438 gms. (1.35 moles) of anhydrous quinine

was added rapidly, the hot solution being filtered to remove mechanical impurities. This solution was then cooled to -10° C. in an ice-salt bath and the precipitated quinine salt collected on a Buchner funnel. This solid was redissolved in fresh hot acetone, re-precipitated, and filtered. This procedure was repeated until the salt had been fractionally recrystallized eight times, of course reducing the quantity of acetone for each crystallization.

This product was then dried over-night and decomposed with 600 cc. of 10 per cent hydrochloric acid, and the acid solution extracted with ether. The ethereal solution was dried over anhydrous sodium sulfate, filtered, the ether distilled off, and the resultant crude, optically-active 2-n-amylbutyric acid distilled under reduced pressure through a modified Claisen flask.

Yield----------62 gms.

B. pt.----------132.5°-133.0° C. at 13 mm.

n_D^{25}----------1.4296

D_o^{25}----------0.8990

$(\alpha)_D^{25}$----------(-) 4.76° (homogeneous)

(b) Esterfication of levo-2-n-Amylbutyric Acid.

$$CH_3.(CH_2)_4.\underset{\text{levo}}{\overset{CH_3}{\overset{|}{C}}}H.CH_2.CO_2H + CH_3.CH_2.OH \xrightarrow[\text{conc. } H_2SO_4]{\text{trace}}$$

$$CH_3.(CH_2)_4.\underset{\text{levo}}{\overset{CH_3}{\overset{|}{C}}}H.CH_2.CO_2.CH_2.CH_3 + HOH$$

A mixture of 62 gms. (0.4 moles) of levo-2-n-amyl-butyric acid (see pages 47-48) 240 cc. of absolute ethyl alcohol, 140 cc. of anhydrous toluene and 1.0 cc. of concentrated sulfuric acid was placed in a one liter flask attached to column RWS and immersed in an air bath at 90°-93° C. The constant-boiling ternary system ethanol-toluene-water came off between 75° C. and 78° C. over a period of eight hours. The flask was then cooled and an additional 120 cc. of ethanol and 60 cc. of toluene were added and the above procedure repeated.

The flask was cooled and the contents transferred to a 500 cc. separatory funnel, washing three times with 30 cc. of 10 per cent potassium carbonate solution. The toluene solution was then separated and dried over anhydrous sodium sulfate, filtered, and the toluene removed through column RWS. The residual liquid was then transferred to an 125 cc. modified Claisen flask and distilled under reduced pressure, collecting 74 gms. of levo-ethyl-2-n-amyl-butyrate.

Yield----------74 gms. or 94%

B. pt.----------118°-119° C. at 35 mm.

D_o^{25}----------0.860

n_D^{25}----------1.4203

$(\alpha)_D^{25}$----------(-)2.10° (homogeneous)

$(M)_D^{25}$----------(-)3.91°

(c) Preparation of levo-3-Methyloctanol-1.

$$4(H) + CH_3.(CH_2)_4.\underset{\displaystyle CH_3}{\underset{|}{CH}}.CH_2.CO_2.CH_2.CH_3 \xrightarrow[C_2H_5OH]{\text{Sodium}}$$

$$CH_3.(CH_2)_4.\underset{\displaystyle CH_3}{\underset{|}{CH}}.CH_2.CH_2.OH + C_2H_5OH$$

A solution of 50 gms. (0.26 moles) of levo-ethyl-2-n-amylbutyrate (see pages 48-49) in 250 cc. of anhydrous ethyl alcohol was added dropwise to a stirred suspension of 80 gms. of clean metallic sodium in 400 cc. of boiling anhydrous benzene contained in a three-liter three-necked round-bottom flask equipped with a mercury-sealed stirrer, a Friedrich reflux condenser and a dropping funnel. The addition was made at such a rate as to just maintain boiling, being complete in two hours. An additional 300 cc. of anhydrous ethanol was added over a period of two hours, and then 300 cc. of 95% ethanol to destroy excess sodium. The solution was stirred for one hour, after which 300 cc. of water were added dropwise and the mixture refluxed for two hours to saponify any unreduced ester. The excess water-alcohol-benzene was distilled off through column RWS, the residual liquor transferred to a separatory funnel and extracted three times with 250 cc. portions of diethyl ether, saving both layers.

The ethereal layer was dried over anhydrous potassium carbonate, filtered, and the ether removed through a stripping column, the carbinol residue then being fractionated

under reduced pressure through column BJS, collecting levo-3-methyloctanol-1.

The aqueous layer was acidified with conc. hydrochloric acid and the recovered optically active acid extracted with 300 cc. of ether in 100 cc. portions, the solution dried over anhydrous sodium sulfate, the ether evaporated off, and the residual acid distilled through a 100 cc. modified Claisen flask under reduced pressure. This acid was then re-esterfied using the procedure given on pages 48-49, the ester reduced again with sodium and alcohol via above procedure, and the yields of carbinol combined. This was repeated three times, after which the following combined yield of levo-3-methyloctanol-1 was realized:

Yield----------29 gms. or 60%

B. pt.----------109°-110° C. at 25 mm.

n_D^{25}----------1.4330

D_4^{25}----------0.827

$(\alpha)_D^{25}$----------(-) 3.77° (homogeneous)

$(M)_D^{25}$----------(-) 5.43°

(d) Preparation of dextro-1-Bromo-3-Methyloctane.

$$CH_3.(CH_2)_4.\underset{\displaystyle CH_3}{CH}.CH_2.CH_2OH + HBr \longrightarrow CH_3.(CH_2)_4.\underset{\displaystyle CH_3}{CH}.CH_2.CH_2.Br + H_2O$$

In a 100 cc. flask was placed 29 gms. (0.15 moles) of levo-3-methyloctanol-1 (see pages 50-51) with a gas inlet tube extending below the surface of the liquid. The flask was immersed in an oil bath at 120°-130° C. and dry hydrogen bromide gas (generated by adding bromine dropwise to boiling tetralin, and passing the HBr evolved through a purification train consisting of napthalene, anhydrous calcium sulfate, phosphoric anhydride, and red phosphorus) was bubbled continuously through the alcohol for 2½ hours. The bromide was then allowed to cool, and the $HBr.H_2O$ layer separated off, the reaction product washed with 50 cc. of water, 50 cc. of 10 per cent potassium carbonate solution, and then with 25 cc. of ice-cold conc. sulfuric acid to remove any unreacted carbinol.

The bromide layer was extracted again with a solution of potassium carbonate, and then dried over anhydrous potassium carbonate, transferred to a 50 cc. modified Claisen flask and distilled under reduced pressure.

Yield----------35 gms. or 88%

B. pt.----------105°-106° C. at 25 mm.

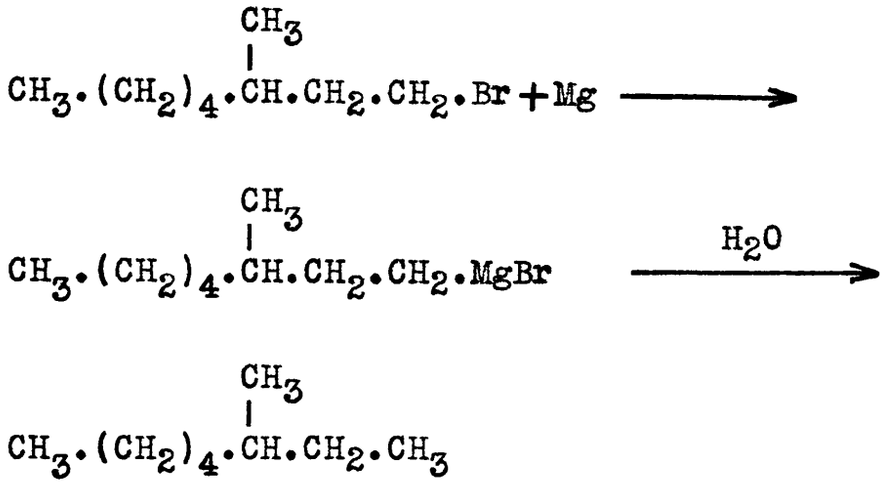
n_D^{25}----------1.4539

D_4^{24}----------1.085

$(\alpha)_D^{25}$----------(+)6.25° (homogeneous)

$(M)_D^{25}$----------(+) 13.35°

(e) Preparation of levo-3-Methyloctane.



A solution of 35 gms. (0.17 moles) of dextro-1-bromo-3-methyloctane (see pages 51-52) in 100 cc. of anhydrous ether was added dropwise over a period of 1½ hours to a mixture of 7 gms. (0.29 moles) of magnesium turnings in 70 cc. of anhydrous diethyl ether contained in a 500 cc. round-bottom three-necked flask equipped with a mercury-seal stirrer, a reflux condenser, a dropping funnel, and an inlet for nitrogen gas. Prior to the addition of the bromide the flask had been swept with nitrogen and one cc. of ethyl bromide added to activate the magnesium.

The reaction with the nonyl bromide was vigorous and the solution turned black. After addition was complete, the solution was refluxed for 1½ hours with constant stirring, after which the flask was cooled, and 125 cc. of 25 per cent hydrochloric acid was added dropwise, over a period of 1½ hours. The product was then steam-distilled out of the flask, the ethereal layer separated, and the aqueous

layer was extracted twice with 25 cc. portions of ether which were then combined with the ether solution. This solution was dried over anhydrous potassium carbonate, filtered, and the ether removed through a stripping column. The residue of hydrocarbon was then placed in a hydrogenation bottle, together with 0.5 gm. of platinum oxide catalyst and shaken for one hour under 3 atmospheres pressure of hydrogen, the catalyst filtered off, and the hydrocarbon fractionated at atmospheric pressure through column BJS, collecting 11 gms. of levo-3-methyloctane.

Yield----------11 gms. or 51%

B. pt.----------142°-143° C. at 760 mm.

n_D^{25}----------1.4045

D_4^{25}----------0.714

$(\alpha)_D^{25}$----------(-) 9.09° (homogeneous)

$(M)_D^{25}$----------(-) 11.6°

(f) Nitration of levo-3-Methyloctane (56).

levorotatory levorotatory

This hydrocarbon was nitrated in two 5½ gms. portions, following the procedure described on pages 39-40 in which nitric acid of specific gravity 1.075 was used at 130° C.

with the variation that the nitrated product was first placed in a flask attached to column BJS and the unreacted hydrocarbon fractionated off, the residue being extracted three times with 15 cc. of aqueous-alcohol (3/1) potassium hydroxide, each extraction lasting at least ½ hour with frequent agitation. The orange-yellow alkaline layer was then extracted once with ether, the ether washed with water, and combined with the alkali-insoluble portion, dried over anhydrous sodium sulfate, filtered, the ether evaporated, and the tertiary nitro compound, 3-nitro-3-methyloctane, fractionated through column BJS under reduced pressure, maintaining a reflux ratio of 50/1.

Yield----------2.8 gms. or 18%

B. pt.----------106.5-107.0° C. at 15 mm.

n_D^{25}----------1.4340

α_D^{25}----------(-) 0.65° (homogeneous)

To ensure freedom from any primary or secondary nitro compounds, this product was re-extracted three times in the same way with 15 cc. portions of 10 per cent aqueous alcoholic (3/1) potassium hydroxide solution, and the product re-fractionated, maintaining a reflux ratio of 50/1.

Yield----------1.8 gms.

B. pt.----------106.0°-106.5° C. at 15 mm.

α_D^{24}----------(-)0.70° (homogeneous)

As can be seen, the optical activity of the product, levo-3-nitro-3-methyloctane, was practically unchanged by this attempt at further purification.

5. Description of Fractionating Columns.

a. Column RWS (Whitmore-Fenske type)

This fractionating column was a modification of the Whitmore-Fenske column, packed with single-turn glass helices. The packed section of the column was 61 cm. (2.0 ft.) long, had an inside diameter of 11 mm. and was filled with tightly packed single-turn glass helices having an inside diameter of 3.0 mm. and an outside diameter of less than 4.0 mm; each helix had been introduced into the tube separately, so that the free space was a minimum.

This part of the column was insulated and heated by means of two telescoped air jackets, the inner one being wound with nichrome-ribbon resistance wire(3.3 ohms/ft), the jacket temperature being controlled by a water-cooled rheostat. The head of the column was of the total-condensation type, with a stop-cock for regulation of the rate of take-off; it also contained a thermometer for measurement of the vapor temperature. The efficiency was determined using a carbon tetrachloride-benzene mixture, and was found to be equivalent to 16 theoretical plates employing a reflux ratio of 20 to 1.

b. Column BJS. (Podbielniak type)

This apparatus was designed and constructed so that

the fractionation of small quantities (5 to 50 cc.) of material could be realized, and was patterned after the Podbielniak type column, which has a very small hold-up, this being the major difficulty in designing a fractionating column for small volumes of material.

The column was built entirely of Pyrex glass, the "packed" portion of the column being 61 cm. (2.0 ft.) in length and having an inside diameter of 3.0 mm. A spiral of gold-plated gold-fill wire, 22-gauge, 2.4 turns per cm., was fitted tightly into this glass tube. This packed section of the column was electrically-heated by means of nichrome-ribbon resistance wire (3.3 ohms/ft.) wound directly on the tube containing the gold-spiral and controlled by means of a 90-ohm water-cooled rheostat.

The whole length of the column, with the exception of the head, was fitted snugly into a sealed vacuum jacket made of pyrex glass and evacuated to 10^{-6} mm. of mercury. The head of the column, which was nothing more than an enlarged extension of the column proper having a side-arm "take-off" tube just above the vacuum jacket, was fitted with a very small 250° C. thermometer. The side-arm held a sleeve-type water condenser.

The efficiency was determined employing a carbon tetrachloride-benzene mixture, and found to be equivalent to 8 theoretical plates using a reflux ratio of 35 to 1, the hold-up being one cc.

SUMMARY

(1) Two new organic compounds, 3-nitro-3-methylheptane and 3-nitro-3-methyloctane, have been prepared by direct nitration (employing Konawalow's sealed-tube, dilute acid method) of the pure, synthetically prepared tertiary hydrocarbons, 3-methylheptane and 3-methyloctane.

(2) Similarly, the optically active forms of these nitroparaffins, dextro-3-nitro-3-methylheptane and levo-3-nitro-3-methyloctane, were prepared by direct nitration of the optically active forms (dextro-3-methylheptane and levo-3-methyloctane) of the above hydrocarbons. This is the first recorded case of formation of an optically active nitro compound, having the entering nitro group replace a hydrogen atom attached to the asymmetric carbon, from an optically active hydrocarbon by direct nitration employing nitric acid as the nitrating agent.

From these facts, together with data compiled by other workers, it has been shown that the nitration of aliphatic hydrocarbons with dilute nitric acid most probably proceeds as follows:

A molecule of hydrocarbon collides with one of true, undissociated nitric acid (HNO_3), forming an activated intermediate, probably through attachment of the HNO_3 molecule to the residual-valence,"face-centered" bond opposite the hydrogen atom to be replaced.

This complex may then decompose in one of two ways:

(a) To give HNO_3 and the original hydrocarbon.

(b) By releasing atomic hydrogen (H.) and (HO.), which may then combine to form water (HO:H), with immediate inversion of the attached hydrocarbon free radical and formation of a nitroparaffin (see p. 32-34 for more complete treatment).

This mechanism most completely satisfies the requirements of the experimental data available on nitration and nitric acid.

Bibliography

1. Konawalow, Ber. 26, 878 (1893); ibid. 28, 1852 (1895); ibid. 29, 2199 (1896).
2. V. Meyer, Ber. 5, 203, 399, 514, 1029, 1034 (1872).
3. Beilstein and Kurbatow, Ber. 13, 1818 (1880); Chem. Soc. Abs. 40, 159 (1881).
4. Konawalow, J. Russ. Phys.-Chem. Soc. 25, 472 (1894); Chem. Soc. Abs. 66 (1), 265 (1894).
5. Worstall, Am. Chem. J. 20, 202 (1898).
6. Markownikow, Ber. 32, 1441 (1899); J. pr. Chem. 59 (2), 556 (1899).
7. Konawalow, Ber. 28, 1852 (1895); Chem. Soc. Abs. 68 (1), 633 (1895); Ber. 29, 2199 (1896).
8. Konawalow, J. Russ. Phys.-Chem. Soc. 38, 109 (1906); Chem. Soc. Abs. 92 (1), 1 (1907).
9. Markownikow, Ber. 32, 1441 (1899); Chem. Soc. Abs. 76 (1), 553 (1899).
10. Francis and Young, J.C.S. 73, 928 (1898).
11. Hass, Hodge and Vanderbilt, Ind. Eng. Chem. 28 339, (1936); C.A. 30, 2918 (1936).
12. Hass and Seigle, Ind. Eng. Chem. 31, 648 (1939); C.A. 33, 4959 (1939).
13. Poni and Costachescu, Ann. Sci. Univ. Jassy 2, 119 (1903); Chem. Soc. Abs. 84 (1), 596 (1903).
14. Reference 4.
15. Worstall, Am. Chem. J. 20, 202 (1898); Chem Soc. Abs. 74, 346 (1898).

16. Konawalow, Ber. 26, 878 (1893); ibid. 28, 1852 (1895); ibid. 29, 2199 (1896); Chem. Zentr. 1905, II, 818 ; ibid. 1906, II, 312.

17. Markownikow, Ber. 32, 1445 (1899); Chem. Soc. Abs. 76 (1), 554 (1899).

18. Markownikow, Ber. 33, 1906 (1900); Chem Soc. Abs. 78 (1), 469 (1900).

19. Konawalow, J. Russ. Phys. - Chem. Soc. 37, 1119 (1905); Chem. Zentr. 1906, I, 737.

20. Konawalow, J. Russ. Phys. - Chem. Soc. 25, 472 (1894); Chem. Soc. Abs. 66 (1), 265 (1894).

21. Worstall, Am. Chem. J. 20, 202 (1898); Chem. Soc. Abs. 74 (1), 346 (1898).

22. Haines and Adkins, J.A.C.S., 47 1419 (1925).

23. Reference 20.

24. Reference 21.

25. Urbanski and Slon, Compt. rend. 204, 870 (1937); C. A. 31, 3868, 6190 (1937).

26. Francis and Young, J.C.S. 73, 928 (1898).

27. Konawalow, J. Russ. Phys.-Chem. Soc. 38, 109 (1906); Chem. Zentr. 1906, II, 312.

28. Worstall, Am. Chem. J. 21, 210 (1899).

29. Konawalow, J. Russ. Phys.-Chem. Soc. 37, 530 (1905); Chem. Soc. Abs. 88 (1), 762 (1905).

30. Markownikow, Ann. 302, 15 (1899); Chem. Soc. Abs. 76 (1), 22 (1899).

31. Markownikow, Ber. 28, 1236 (1895); Ann. 307, 335 (1899); Chem. Soc. Abs. 76 (1), 799 (1899); J. Russ. Phys.-Chem. Soc. 31, 214 (1899); Chem. Zentr. 1899, I, 1211.

32. Nametkin, J. Russ. Phys.-Chem. Soc. 43, 1603 (1911).

33. Markownikow, Ann. 302, 15 (1898).

34. Nametkin, J. Russ. Phys.-Chem. Soc. 42, 581 (1910); Chem. Soc. Abs. 98 (1), 829 (1910).

35. Markownikow, J. Russ. Phys.-Chem. Soc. 35, 1033 (1903); Ann. 341, 130 (1905).

36. Nametkin, J. Russ. Phys.-Chem. Soc. 42, 691 (1910).

37. Konawalow and Jebenko, J. Russ. Phys.-Chem. Soc. 31, 1027 (1899); Chem. Soc. Abs. 78 (1), 324 (1900); J. Russ. Phys.-Chem. Soc. 38, 449 (1906); Chem. Soc. Abs. 92 (1), 203 (1907).

38. Konawalow and Kikina, J. Russ. Phys.-Chem. Soc. 34, 935 (1902).

39. Nametkin, J. Russ. Phys.-Chem. Soc. 47, 409 (1915).

40. Hantzsch, Ber.58, 954 (1925).

41. Brunetti and Ollano, Atti. accad. Lincei 13, 52 (1931).

42. Groggins, "Unit Processes in Organic Synthesis", p. 9, 1935 ed.

43. Jones, Carnegie Institution of Washington, Publication 60, 93 (1907).

44. Usanovich, J. Gen. Chem. (U.S.S.R.) 10, 219 (1940); C. A. 34, 7285 (1940); see also C. A. 33, 6688 (1939).

45. Bronsted, Ber. 61B, 2049 (1928); C. A. 22, 4323 (1928); Klages, Z. Electrochem. 39, 663 (1933); C. A. 27, 5619 (1933).

46. Lauer and Oda, J. prakt. Chem. 144, 176 (1936); C. A. 30, 3791 (1936).

47. Reference 25.

48. Lewis, J.A.C.S. 38, 762 (1916).

49. Gilman, "Organic Chemistry" page 114 (1938 ed.)

50. McCleary and Degering, Ind. Eng. Chem. 30, 64 (1938).

51. Reference 12.

52. Hass and Patterson, Ind. Eng. Chem. 30, 67 (1938); C. A. 32, 1648 (1938).

53. Ewell, Ind. Eng. Chem. 31, 272 (1939).

54. Reference 17.

55. Whitmore, J.A.C.S. 54, 3274 (1932).

56. Stevens and Schiessler, J. A. C. S. 62, 2885 (1940).

57. Brown, Kharasch and Chao, from a paper presented to the Division of Organic Chemistry at Detroit, Mich., September, 1940. Abstract of papers, pages 57-59.

58. Lewis, "Valence and Structure of Atoms and Molecules", Chemical Catalog Co., New York, p. 113 (1923).

59. Olson, J. Chem. Phys. 1, 418 (1933).

60. Reference 39.

61. Whitmore, Popkin, Bernstein, and Wilkins, J.A.C.S. 63, 124 (1941).

63. von Rissegehm, Bull. soc. chim. Belg. 39, 369 (1930).

64. Duveen and Kenyon, Bull. soc. chim. 5, 1123 (1938).

65. Welt, Compt. rend. Acad. 119, 745 (1894).

66. Levene and Marker, J. Biol. Chem. XCI,1, 95 (1931).

[Reprinted from the Journal of the American Chemical Society, 62, 2885 (1940).]

THE NITRATION OF ALIPHATIC HYDROCARBONS

Sir:

While the nitration of hydrocarbons is one of the oldest reactions known, it is still one of the least understood. Recently nitration of simple saturated hydrocarbons has been carried out in the vapor phase at elevated temperatures,[1] a reaction said to involve free radicals.[2] Since little is known about the mechanism of this nitration in the liquid phase, we wish to report that nitration of *levo*-3-methyl-octane yields *levo*-3-methyl-3-nitro-octane.[3]

The mechanism of this nitration is still not clear. However a survey of the literature reveals the following pertinent facts:

A. Tertiary hydrogen atoms are generally the most easily replaced.[4]

B. Nitration of neohexane proceeds without rearrangement yielding 3,3-dimethyl-2-nitro-butane.[5]

C. Nitration of camphane (caged structure) yields secondary nitro compounds in place of the expected tertiary.[6] indicating an inversion mechanism.[7]

For the empirical equation $C_9H_{20} + NO_2 \rightarrow C_9H_{19}NO_2 + H$, several mechanisms can be advanced:

1. Replacement by removal of the hydrogen as a proton. This would appear implausible from (A) above. The well-known electron-repelling

(1) Haas, Hodge and Vanderbilt, *Ind. Eng. Chem.*, **28**, 339 (1936).

(2) McCleary and Degering, *ibid.*, **30**, 64 (1938), Seigle and Haas, *ibid.*, **31**, 648 (1939).

(3) It is not yet possible to say whether or not partial racemization occurred.

(4) Konowalov, *Ber.*, **28**, 1855 (1895).

(5) Markownikov, *Chem. Zentr.*, **70**, II, 473 (1899); *Ber.*, **33**, 1906 (1900).

(6) Nametkin, *J. Russ. Phys.-Chem. Soc.*, **47**, 409 (1915).

(7) Bartlett and Knox, THIS JOURNAL, **61**, 3184 (1939).