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THE ACTION OF NITROGEN TRIOXIDE ON PINENE.

by

Ernest Wayne Rembert

A

THESIS

submitted to the faculty of

THE SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY
OF MISSOURI

in partial fulfillment of the work required for the

DEGREE OF

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1921

Approved by

Professor of Chemistry.

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INTRODUCTION.

The action of nitrous acid on pinene was first studied by Pesci and Bettelli¹ in 1885. They obtained an oil, which, when treated with NH_4OH and steam distilled gave a product of the formula $\text{C}_{10}\text{H}_{16}\text{NO}_2$. At this point the investigation was discontinued.

It is the purpose of this work to show the true mechanism of the reaction and also to establish the formula and nature of the products obtained.

The author takes this opportunity to express his appreciation for the kind assistance which he has received from the various members of the Chemistry Department and the Library of the Missouri School of Mines and Metallurgy.

EXPERIMENTAL PART.

1. Pinene:-

The pinene used in the subsequent experiments was obtained from new turpentine by shaking with one-half its volume of 5% NaOH solution, separating from the water layer and dehydrating over CaCl_2 . This product was then distilled and the fraction boiling at 156° - 157° taken.

It was not necessary to purify the pinene by precipitation as the nitrosyl chloride and regenerating with aniline because of the nature of the final products after treatment with N_2O_3 .

2. Treatment with N_2O_3 .

A 1 liter Erlenmeyer flask was fitted with a thermometer, a dropping funnel and a mechanical stirrer. The flask was placed in a freezing bath which was maintained between -10° and -12° C.

550 c.c. of 6N H_2SO_4 were introduced into the flask and allowed to cool to a temperature of -10° C. 100 gms. of pinene were poured into the acid and allowed to come to the above temperature. Then the stirrer was started and 125 gms. of pure NaNO_2 in 275 c.c. of water, were added dropwise through the dropping funnel,

care being taken that the temperature of the contents of the flask did not rise above 0° C.

The heat liberated was considerable and it was quite difficult to hold the contents of the flask at 0°. For proper temperature control, it was found necessary to add the NaNO_2 solution at such a speed as to finish the process in not less than four hours and preferably in five hours. If the temperature runs too high, the mass gums and much N_2O_3 is lost, resulting in a low yield.

After the first 10 c.c. of the NaNO_2 solution is added, the contents of the flask assume a deep green color which later turns to a dark greenish brown.

After the whole of the NaNO_2 solution has been added, the stirrer is allowed to run for about fifteen minutes and is then stopped. The contents of the flask are poured into a separatory funnel and the dark green, oily layer which rises to the top is separated from the water solution of NaHSO_4 .

The dark green oil was then washed four or five times with ice water by shaking in the separatory funnel. It was noticed that the oil settles to the

bottom in the wash water.

Upon attempting to distill this oil, it was found to decompose rapidly below 100° C, and, slightly above that temperature, to completely carbonize. Therefore, another method of purification was necessary. The oil is practically insoluble in water and miscible in all proportions with CH_3OH , glacial CH_3COOH , $\text{C}_2\text{H}_5\text{OH}$, C_6H_6 , $(\text{CH}_3)_2\text{CO}$, $(\text{C}_2\text{H}_5)_2\text{O}$, CS_2 , CCl_4 , and CHCl_3 .

3. Fractional precipitation of the oil.

100 gms. of the oil were dissolved in 200 c.c. of CH_3OH and placed in a separatory funnel. Water was added until the solution became just turbid. Then two c.c. were added in excess. The mixture was allowed to stand until the layers completely separated and the lower layer then drawn off. About 15 c.c. of a pale green oil were obtained from this step.

This oil was lighter than water and the greater part distilled between 156° - 158° C., the boiling point of pinene. Analyses showed a carbon content of about 88%, which bore out the conclusion that the first precipitated product was pinene.

That there is a marked difference in the solubility of the components of the green oil in alcohol-

water solution, is shown by the fact that, at this point, about 1/2 c.c. of H₂O was added before the solution again became turbid.

5 c.c. of H₂O were then added and the mixture allowed to separate into two layers. The lower layer, amounting to about 70 c.c., was drawn off, re-dissolved in 200 c.c. of CH₃OH and the above process repeated. The second fraction from this precipitation is then dried over CaCl₂. About 60 c.c. of the oil were obtained from the second precipitation with a removal of practically all of the pinene.

The oil at first is greenish brown in appearance, but upon standing for two or three days changes to a light straw. It is slightly heavier than water in which it is practically insoluble. It is miscible in all proportions with all of the common organic solvents. It cannot be distilled, decomposition beginning about 80° C. It is volatile in steam.

Analysis showed its formula to be C₁₀H₁₆NO₂. The results are as follows:

	Found	Calculated.
Carbon	65.9	66.0
Hydrogen	9.4	8.8

	Found	Calculated.
Nitrogen	6.9	7.7
Oxygen	17.8	17.5

Carbon and hydrogen were determined by the usual combustion method, nitrogen by the modified Kjeldahl method and oxygen by difference. Considerable difficulty was experienced in the determination of nitrogen due to the rapidity with which the compound decomposed with H_2SO_4 . A slight loss was unavoidable.

25 c.c. of the oil were dissolved in 50 c.c. of glacial acetic acid and cooled to $0^{\circ}C$. 23 gms. of bromine (7.5 c.c.) were added slowly with constant stirring. After the bromine was added, the solution was diluted with ice water and the heavy oil separated. It was washed several times with cold CH_3OH , then dissolved in warm alcohol and allowed to crystallize.

The portion of the original oil remaining in the alcohol-water solution, when precipitated, gave no evidence of being a pure compound, so it was discarded.

4. The action of bases on the oil from the first treatment.

100 gms. of the oil were added to 75 c.c. of 15% ammonium hydroxide and allowed to stand three or four hours with frequent shaking. The contents require

a deep red color, similar to that of bromine. The mixture was then extracted with ether and the layers separated.

It was found advisable to use 15% ammonia solution in that a stronger solution caused too great an evolution of heat.

The ether layer was shaken with dilute HCl and separated. The ether was then distilled off and the residue distilled in steam. Unchanged pinene was the first to distill. Later the oil in the distillate settles to the bottom of the container.

This oil proved to be identical with that obtained from the second fraction precipitated from the alcohol-water solution mentioned above, corresponding to the formula $C_{10}H_{16}NO_2$. Pesci & Bettelli¹ obtained this product by a similar process.

The ammonia layer was cooled to about 0° and made just acid with HCl. Considerable heat was liberated and some gas evolved. A deep red wax like substance settles out. This was washed with distilled water and dried over H_2SO_4 .

Analysis showed it to have the formula $C_{10}H_{17}N_3O_4$. The results are as follows:

	Found	Calculated.
Carbon	49.3	49.4
Hydrogen	7.3	7.0
Nitrogen	15.9	17.3
Oxygen	27.5	26.3

The same difficulty was experienced in the determination of nitrogen with this compound as with the compound $C_{10}H_{16}NO_2$.

A portion of the compound $C_{10}H_{17}N_3O_4$ was finely divided and allowed to stand in contact with a large excess of concentrated ammonium hydroxide for several days. It was noticed that only a small amount of the substance redissolved. Instead, a white solid remained in the bottom of the flask. The liquid was decanted and the residue washed well with water by decantation. It was then filtered and dried in the dessicator.

Analysis showed the solid to have the formula $C_{10}H_{16}N_2O_3$. Results:-

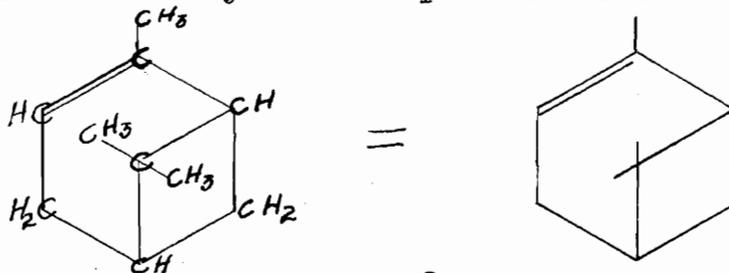
	Found	Calculated.
Carbon	56.1	56.6
Hydrogen	7.9	7.6
Nitrogen	12.6	13.2
Oxygen	23.4	22.6

There is no doubt that this product contained a small quantity of the substance $C_{10}H_{17}N_3O_4$. The latter substance when treated with NH_4OH formed in small globules which soon became coated with the white solid. The best results were obtained by grinding it in a mortar, together with a paste of $(NH_4)_2CO_3$ and NH_4OH , but this process required several hours.

No melting point could be obtained, the substance decomposing about $60^{\circ} C$.

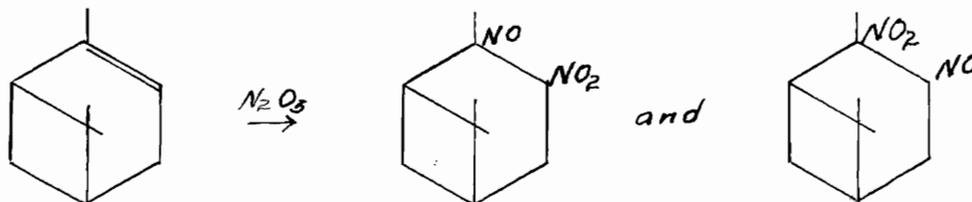
THEORETICAL CONSIDERATIONS.

In the present discussion, Baeyers formula for pinene will be accepted. For convenience we shall use the symbolic representation

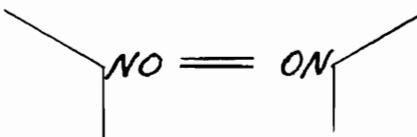


Wieland² has shown that N_2O_3 will break the double bond of an unsaturated compound and substitute the groups NO_2 and NO . The so-called "Nitrite" of phellanthrene was isolated by Pesci.³

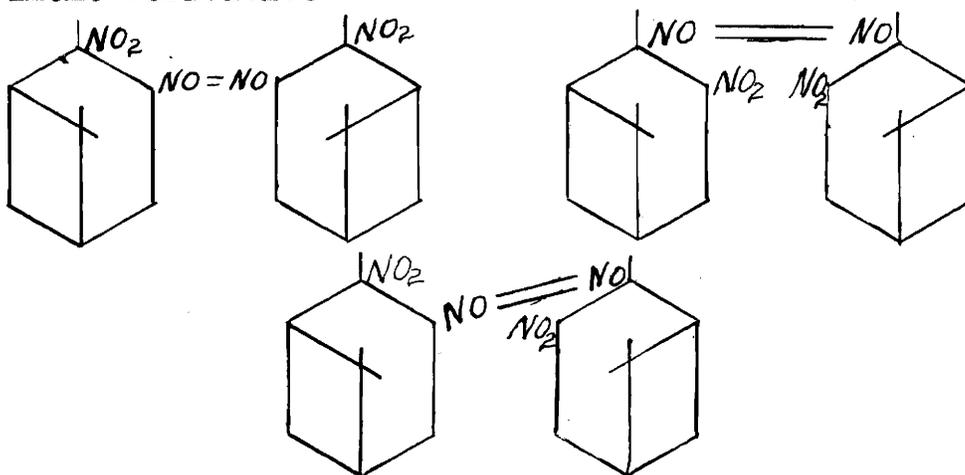
With these points in view, the first step in the reaction may be considered as forming the two dynamic isomers



Wieland² has also shown that the nitroso groups often combine to the bi-molecular form:-



This being the case, there appears three possible bi-molecular isomers in the case of the pinene derivative

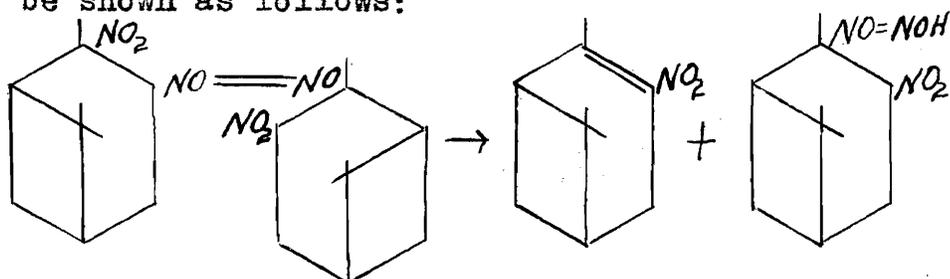


Of the three possible isomers, it appears that the latter would be the most unstable, due to the lack of symmetry of the molecular structure. Also, there is no apparent reason why the positions of NO and NO₂ groups entering the double bond should be fixed to any definite carbon atom connected by this double bond. Therefore, it may be considered that equal quantities of the two possible mono-molecular isomers are formed with a complete formation of the unsymmetrical bi-molecular compound.

As was stated above, this compound is unstable

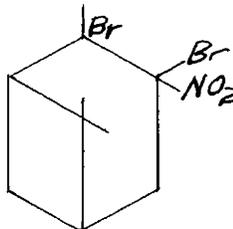
and decomposes completely upon standing several days, or within several hours in the presence of a base.

The rupture of the bi-molecular formula may be shown as follows:

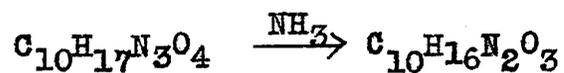


It is quite apparent that the rupture must occur in the bi-molecular formula, as shown, in order that an H atom be available.

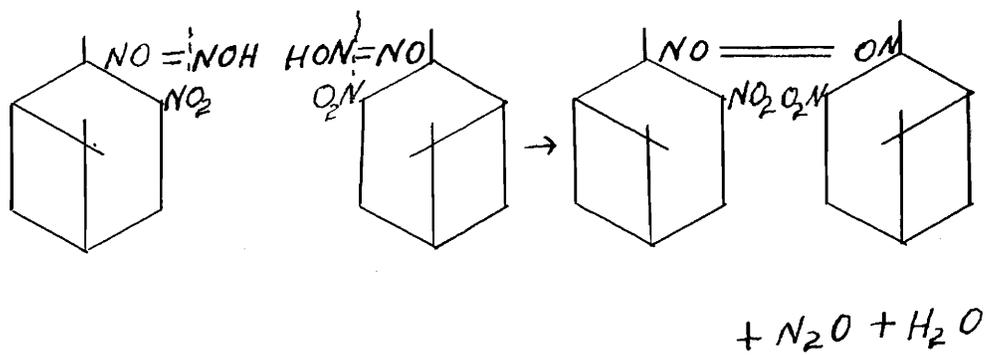
The nitro compound was shown to contain one double bond by the formation of a di-brom derivative



The reaction



may be explained structurally as follows:



SUMMARY.

1. It has been shown that N_2O_3 reacts with pinene to give two possible monomolecular isomers as described.
2. These isomers are considered to form in equal quantities and form an unsymmetrical bi-molecular compound with formula as shown.
3. This bi-molecular compound is unstable and decomposes into two compounds, $C_{10}H_{16}NO_2$ and $C_{10}H_{16}N_3O_4$.
4. The compound $C_{10}H_{16}N_3O_4$ when treated with NH_4OH decomposes to form the symmetrical bi-molecular compound $(C_{10}H_{16}N_2O_3)_2$ as shown.

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Gazetta Chimica Italiana; 16:337
2. Wieland
Annalen; 328:154; 329:225; 340:63
3. Pesci
Gazetta Chimica Italiana; 16:226