THE ACYLATION OF THE SECONDARY NITROPARAFFINES AND A STUDY OF THEIR REARRANGEMENT.

A THESIS

by

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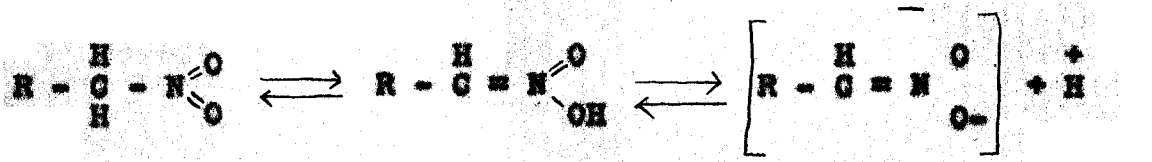
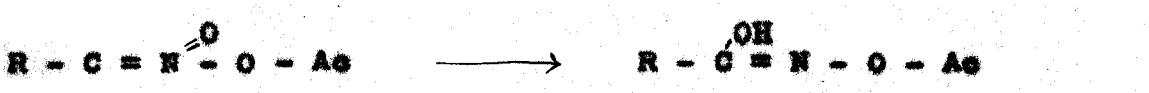
The Acylation of the Secondary Nitroparaffines and a Study of their Rearrangement.

As is well known, the primary and secondary nitroparaffines, through a tautomeric rearrangement of a hydrogen atom, are capable of assuming a structure which is acid in character. As a result, these substances interact with alkalies to form salts



It can readily be seen that such behavior is not possible with the tertiary derivatives, owing to the absence of the necessary hydrogen atom.

The sodium and potassium salts, or, most readily, the silver salts of these nitroparaffines, will react with the acyl chlorides to produce esters. It was, however, shown by L. W. Jones[1] that in the case of the primary nitroparaffines, these esters suffered a rearrangement due to internal oxidation and reduction as follows



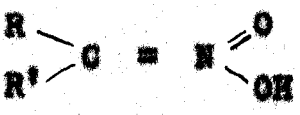
There was thus obtained a hydroxamic acid ester. Not only was some of this material isolated, but

[1] Amer. Chem. Jr. 20, 1.

also a number of secondary products resulting from its further interaction with a portion of the original substances.

It might also be added, that although this rearrangement apparently takes place more readily with the esters, Bamburger and Rust[2] later accomplished the same result with a few of the free-iso-nitroparafines. Thus by boiling phenyl nitro methane (iso form) with concentrated sulphuric acid, the resulting mixture gave a red coloration with ferric chloride indicating benzhydroxamic acid. In the case of p-nitro-phenyl nitro methane, the corresponding hydroxamic acid was isolated.

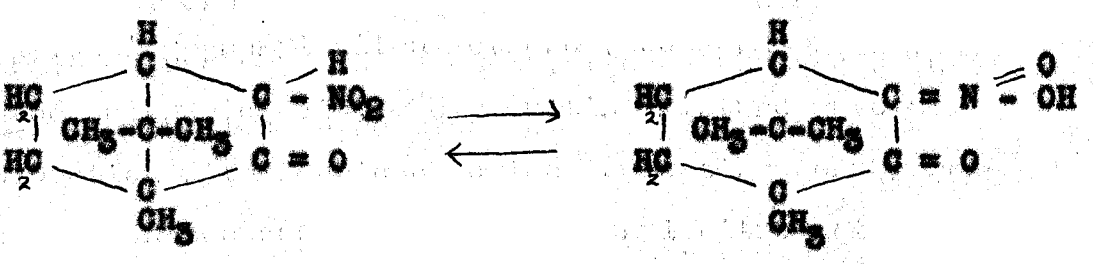
From their formulae, it becomes evident that such an internal rearrangement to produce a hydroxamic acid derivative is only possible with a primary nitroparaffine. A secondary compound, as expressed by the general formula



having no hydrogen atom attached to the N carbon atom would not be capable of rearrangement and, therefore, should yield the acyl esters without difficulty. In the following experiments an attempt has been made to vary the nature of the substituent radicals as widely as possible, including halogens, alkyl and aryl groups.

[2] Ber. 35, 47.

It was found that one example intended for investigation, has already been recorded and confirms the above view. Lowry[3] prepared both the acetyl and benzoyl esters of nitro-camphor. This can be considered a secondary nitroparaffine in which R and R' are both a part of the same ring.



Normal Form Iso Form

Experimental

Benzoyl Ester of Secondary Nitropropane.

4 g. of the freshly prepared sodium salt of secondary nitropropane were suspended in absolute ether and 5 g. of benzoyl chloride added slowly, keeping the mixture well cooled. A deep blue color was produced indicating the formation of a pseudonitrol. After standing for a couple hours, the ether solution was filtered from the sodium chloride and evaporated in vacuo. After standing several days, the residue in the dessicator lost its blue color and changed to a brown oil mixed with a large amount of benzoic acid crystals. In order to remove these, it was redissolved in ether and shaken with a dilute

[3] Jr. Chem. Soc. 73, 999.

solution of sodium hydroxide. The ether layer was dried and evaporated. A small amount of a light yellow oil remained which gave a qualitative test for nitrogen. It decomposed gradually on standing, depositing more crystals of benzoic acid so that a sufficiently pure sample for analysis could not be obtained. It possessed a strong basic odor and appeared to be the desired ester.

Among the typical secondary nitroparaffines of the aromatic type, diphenyl nitro methane was selected as suitable for investigation. Attempts to prepare this substance in sufficient quantity have not yet been successful, but the results obtained by the trial of two different methods are of sufficient interest to be recorded here.

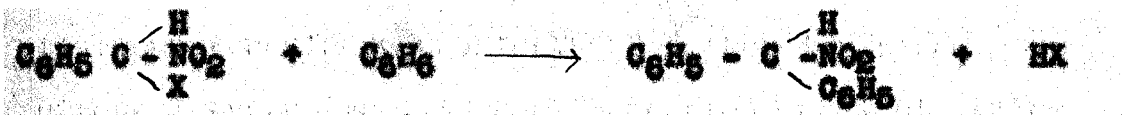
Diphenyl nitro methane is described by Konowalow[4], who prepared it by direct nitration of diphenyl methane. This method was found to produce only very small yields and so was discarded. Two other methods appeared possible:

(a) By usual method of nitroparaffine preparation - action of silver nitrite on the halide of the hydrocarbon,

$$(C_6H_5)_2C\begin{matrix}H\\X\end{matrix} + AgNO_2 \longrightarrow (C_6H_5)_2C\begin{matrix}H\\NO_2\end{matrix} + AgX.$$

(b) By starting with a halogen derivative of monophenyl nitro methane and introducing a second phenyl group by means of the Friedel and Craft reaction.

[4] Jour. Chem. Soc. of Russ. 26, 77.



Of these two reactions, the former seemed less promising of success than the latter. This will be understood from the results of this reaction in other similar cases. From such data, two general statements may be formulated.

(1) The higher the molecular weight of the hydrocarbon radical, the lower the yield of the nitroparaffine.

(2) The nitration of a secondary carbon atom gives a smaller yield than the nitration of a primary carbon atom.

The compound in question possess both of these disadvantages. Furthermore, monophenyl nitro methane which was prepared according to this method of Hollemen[5], after several failures by others[6], gave only a 20% yield.

The diphenyl derivative was investigated as follows: 8 g. diphenyl brom methane were dissolved in 50 c.c. of absolute ether and 5 g. of dry powdered silver nitrite were added. The mixture was warmed for five hours with a reflux condenser. Considerable evolution of brown fumes was observed. The silver bromide was then filtered off and the ether solution evaporated in vacuo. A solid mass of lemon yellow color, weighing 7 g. was obtained. The color was due to a small amount of oil which was almost completely eliminated by pressing on a porous plate. The remainder was removed by washing with a small amount of ether. The white residue was then recrystallized

[5] Recueil d Trav. de Chim. 13, 403.

[6] J.J. Van Renesse, Ber. 9, 1454, and Brunner, Ber. 9, 1744.

from hot alcohol. Fine crystals were obtained which melted at 109° and were identified as benzhydrol ether. The yield of purified product was 3.5 g. By extracting the ether by means of a porous plate a small amount of yellow oil was obtained which was shown to contain nitrogen and was probably the nitro derivative.

A second trial was made, using the same quantities of material as above, but with dry benzol as the solvent in place of ether. In this case only 1.5 g. of benzhydrol ether was obtained and 4 g. of an impure yellow oil containing nitrogen. This was evidently the nitro derivative for it acted with sodium hydroxide and sodium ethylate to give crystals of a salt from which the oil could be recovered by addition of acid.

The formation of benzhydrol ether is very readily explained on the basis of the methylene dissociation theory of Nef. The diphenyl brom methane is first dissociated as follows:

$$(C_6H_5)_2C\begin{matrix}H\\Br\end{matrix} \longrightarrow (C_6H_5)_2C< \quad + \quad HBr$$

The hydrobromic acid which is liberated then interacts with the silver nitrite, producing nitrous acid which yields water and nitrogen trioxide.

$$2HBr + 2AgNO_2 \longrightarrow 2AgBr + H_2O + N_2O_3$$

This accounts for the brown fumes evolved. The water formed here, now combines with the methylene derivative for form the benzhydrol ether.

$$2(C_6H_5)_2C\!<\!\!\!\diagup \;+\; H_2O \longrightarrow (C_6H_5)_2C\!<\!\!\!\begin{matrix}H\\ \diagdown O\\ \diagup\end{matrix}\!\!>C(C_6H_5)_2$$

It is to be noted that, since the dissociation of two molecules of diphenyl brom methane is necessary for the production of each one molecule of water, the formation of the ether and not of benzhydrol itself is explained. These results agree with the work of Nef[7] on the same compound. He found that diphenyl brom methane, on standing with cold water, gave benzhydrol and hydrobromic acid, while with boiling water and a little alkali the ether was formed. Benzhydrol is also converted into the ether by heating to its boiling point (298°) for a long time. This is unique in that it is the only example of direct conversion of an alcohol to an ether by heating alone.

In taking up the second possible method of preparing diphenyl nitro methane, i.e., by phenylation of phenyl brom nitro methane, it was found that no mention of this latter compound could be found in the literature. It was made by bromination of phenyl nitro methane according to the method of Scholl[8] for the simple methyl derivative.

The phenyl nitro methane was converted into its sodium salt by means of sodium ethylate. 30 g. of this salt, dried and finely powdered, were added gradually

[7] Ann. d. Chem. 298, 237.

[8] Ber. 29, 1924.

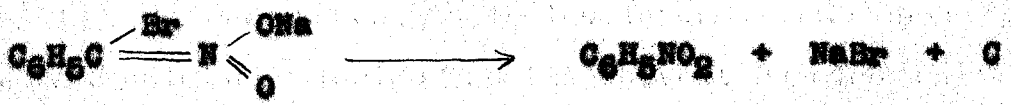
to a solution of 30 g. bromine in 200 c.c. of carbon bisulphide. The solution was kept cool with ice during the experiment. After all the salt had been added the mixture was shaken vigorously for ten minutes. Water was then added to dissolve the sodium bromide and a stream of sulphur dioxide was passed into the mixture until the slight excess of bromine had been reduced and the solution became colorless.

The carbon bisulphide layer was the separated, dried over calcium chloride and the solvent removed by distillation. A dark yellowish red oil remained. The lower fraction produced crystals, part of which formed in the condenser while the remainder were formed suspended in the oily distillate. These were removed by filtering with a suction pump after cooling the mixture in an ice bath. The crystals, ammounting to 4. g. were identified as benzoic acid.

The oil was redistilled, boiling constantly at 124.5° under a pressure of 11.5 m.m. 16g. of phenyl brom nitro methane were obtained. It is a heavy oil of pale straw collor, possessing a spicy odor resembling cinnamon.

For analysis, it was converted into its sodium salt by treatment with the calculated amount of sodium dissolved in absolute alcohol. The salt is precipitated in a white crystalline form. It is collected on a filter and washed with alcohol and ether. It tends

to turn light yellow and later pink. It was hurriedly placed in a vacuum dessicator but after standing about ten minutes, suddenly decomposed with a puff which raised the lid of the dessicator and sent forth a dense cloud of white smoke, no doubt, particles of sodium bromide. There remained a quantity of carbon and a dark yellow oil, having odor of nitrobenzene. The possible decomposition is as follows:

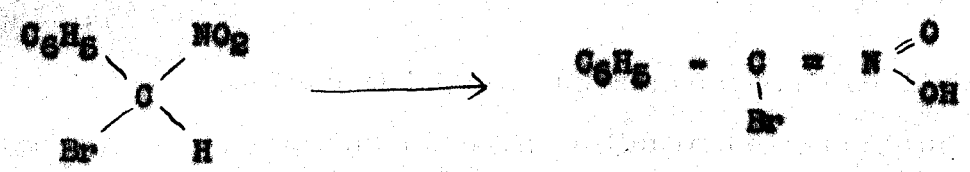


A second quantity of the salt was prepared and by rapid working a sample for analysis was obtained although it had turned slightly yellow before it could be weighed. The remainder exploded before a check could be run.

Analysis .3536 g. of salt gave .1050g. Na_2SO_4

Calculated for $C_7H_5BrNO_2Na$ - Na 9.66% Found 9.51%

An interesting feature of the free nitro derivative is that it contains an asymmetric carbon atom, but if an attempt were made to utilize its acid forming properties to resolve its active antimeres it would lose its asymmetry due to the shift of the hydrogen atom.



The phenylation of this substance by the Friedel and Craft reaction has not yet been tried.

Dinitro Methane.

Although this substance is not a secondary nitroparaffine, its action with benzoyl chloride offers some interesting results which have not yet been fully determined.

The potassium salt was made according to the method of Duden[9] starting with tribrom aniline. The potassium salt was then converted into the silver salt by double decomposition with silver nitrate in water solution. The silver salt was used in order to obtain a more rapid and effective reaction with benzoyl chloride.

5 g. of the silver salt were suspended in 35 c.c. of ether (absolute) and 3.2 g. benzoyl chloride. A slight boiling, which occurs at the beginning is stopped by cooling in an ice bath. At the end of about two weeks standing with occasional stirring, the odor of the benzoyl chloride had disappeared. During this time the contents of the flask were protected from moisture by a calcium chloride tube. The ether solution, which is now deep yellow, was filtered from the silver chloride. The weight of the latter showed a practically quantitative interaction.

Evaporation of the ether solution in vacuo, leaves a yellow oil containing crystals of benzoic acid. After standing a short while it began to decompose giving off a gas. The oild was transferred to a distilling flask and heated to 140° under 20 m.m. pressure, the vapors being passed through a U tube immersed in a freezing mixture.

[9]Ber. 26, 3004.

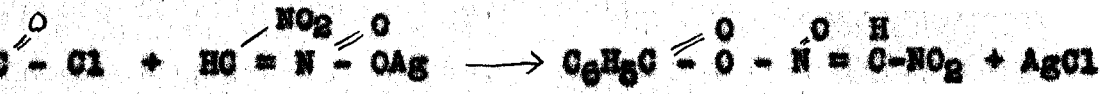
Nothing could be condensed in the tube. Removing the vacuum and continuing the distillation with barium hydroxide solution in the U tube, it was shown that carbon dioxide was present in the gas.

The entire experiment was repeated with anhydrous benzene as the solvent. The entire solution, after removal of the silver chloride, was placed in a distilling flask and distilled in a stream of carbon dioxide. The apparatus was so arranged as to collect any gaseous decomposition products, other than CO_2, over potassium hydroxide solution in a nitrometer. After the benzene had been distilled off, the oil began to decompose about 117° with slow evolution of gas, and continued until around 250°, when benzoic acid began to distil. As will be seen later, the gas obtained could only be nitrogen or nitrous oxide. It was, therefore, transferred to an explosion pippette and mixed with an equal volume of hydrogen. There was no effect however on the passage of the spark, so it was concluded to be nitrogen. Less than half the calculated quantity of nitrogen was obtained. From the residue in the distilling flask, benzoic acid was first extracted with ligroin. Then, by means of ether, a small quantity of oil was obtained which had a pleasant, perfume-like, odor, but has not yet been identified. It was probably a benzoic ester, as the odor resembled, but was not identical with, methyl benzoate.

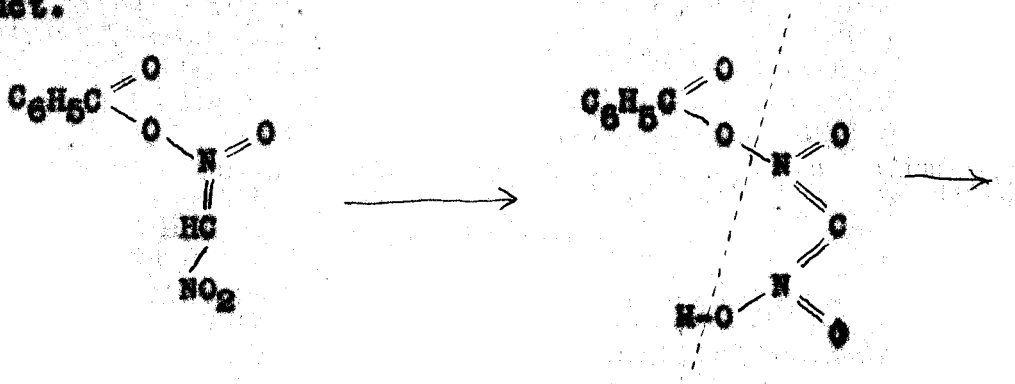
The following reactions are offered as a tentative explanation of the above results until more

conclusive evidence has been obtained.

(a) The quantitative separation of silver chloride shows that ester is the first product formed.



(b) The separation of benzoic acid can occur in only one way, since there remains in the compound but a single H atom outside the benzene ring. If we subtract the formula of benzoic acid, there remains CN_2O_3 from which we must again subtract carbon dioxide leaving either N_2O or N_2 and O. Two other facts must be considered. Only half the molecules present are decomposing in this manner, since the nitrogen obtained is not the total amount present. Also, since free oxygen was not obtained it must have combined with the remaining molecules to form some oxidation product.



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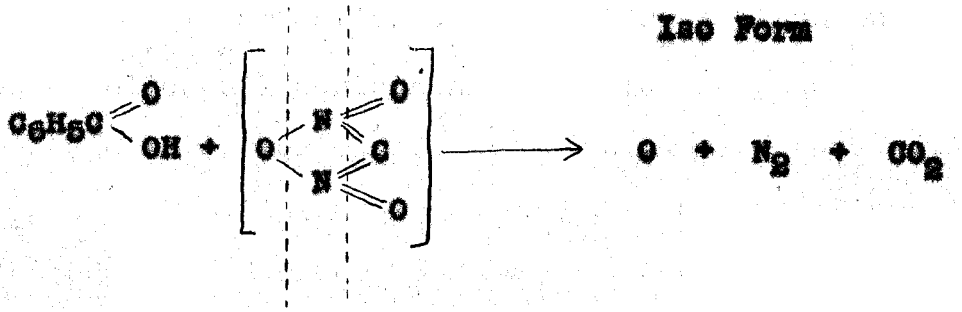
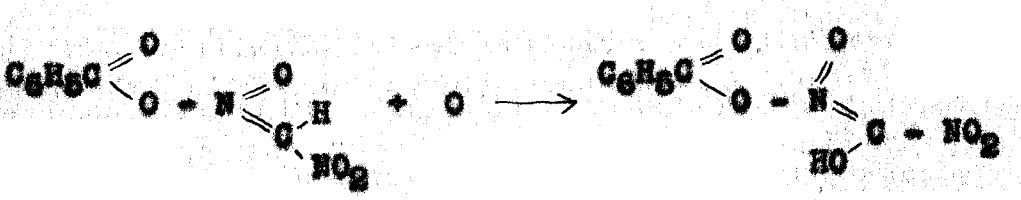


(2)



This substance which is alcoholic may combine with some of the benzoic acid already formed, to produce an ester thus accounting for the oil obtained.