LVIII.—*Conversion of Aliphatic Nitrites into Nitro-compounds.*

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One of us has already shown (Neogi, T., 1914, **105**, 2371) that the idea of tautomerism cannot properly be applied to the case of nitrites and nitro-compounds, and has advanced the theory that the formation of aliphatic nitrites and nitro-compounds may be attributed to two causes, namely, (1) isomeric conversion of nitrites into nitro-compounds, and (2) formation of unstable intermediate additive compounds. The present investigation was undertaken with the object of finding experimental evidence of the conversion of aliphatic nitrites into nitro-compounds. Experiments show that aliphatic nitrites are partly converted into the corresponding nitro-compounds by the action of heat.

Conversion of Ethyl Nitrite into Nitroethane.

The apparatus employed in the case of methyl and ethyl nitrites was the same. The solution of the nitrite in paraffin oil was placed in a flask provided with an upright spiral condenser, which in turn was connected with a combustion tube about 90 cm. long, filled with asbestos-wool (in order to expose a large surface to the gaseous nitrites), and heated in an asbestos box provided with a thermometer. The gaseous nitrite was carried into the tube by means of a slow stream of dry carbon dioxide. The nitro-compound was collected in a U-tube immersed in cold water, and the escaping nitrite in absolute alcohol or methyl alcohol cooled in ice-water.

Fifteen or 20 c.c. of the nitrite solution were used at a time. A 25 per cent. solution is convenient, and a 50 per cent. solution loses nitrite very rapidly. As the gaseous nitrite remains only momentarily in contact with the heated asbestos, the yield of the nitro-compound is small, the greater portion of the nitrite escaping conversion. Within four or five hours the greater part of the dissolved nitrite passes through the heated tube. The oily nitro-compound was easily recognised by the formation of the sodium compound on the addition of alcoholic sodium hydroxide solution.* The nitro-compound was also reduced to the corresponding amine, which was converted into the platinichloride. (Found, Pt = 38·79. Calc., Pt = 39·00 per cent.)

The conversion commenced at 100°, and was fairly rapid at 120—130°, when oily drops began to collect in the empty U-tube. At the end of four to five hours about 1 c.c. of the liquid collected, which responded very readily to the alcoholic sodium hydroxide test. If the temperature is raised to about 135—150°, acetaldehyde and acetic acid are produced along with the nitro-compound. At 150—180° the acid is the main product of the decomposition. The formation of the aldehyde and the acid is readily explained by the fact that at a higher temperature the nitrite dissociates into alcohol and nitrous acid, the latter decomposing into nitric acid, and the higher oxides of nitrogen which oxidise the alcohol to the aldehyde and the acid. The best yield of the nitro-compound is obtained at 120—130°.

In order to ascertain if a better yield is obtained when an alcoholic solution of the nitrite is heated in a sealed tube, 10 c.c. of the solution were sealed in a glass tube and heated in a furnace. During the act of sealing, the part of the tube containing the solution should be immersed in a freezing mixture, as otherwise explosions take place. The yield, however, was not very satisfactory. When heated at 100° for five to six hours the solution, after distilling off the unchanged nitrite and alcohol, gave about 1 c.c. of liquid, which responded to the test for a nitro-paraffin and boiled at 98—104°. Owing to the admixture of alcohol, the actual boiling point was lowered. If, however, the solution was heated to 150° for twelve to fifteen hours, the tube was found to contain acetic acid, formed by the oxidation of the alcohol by nitric acid and higher oxides of nitrogen produced from the decomposition of the nitrite, besides free nitrite. The proportion of the nitro-compound was very small.†

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* Blank experiments were made with nitrites, nitrates, alcohols, aldehydes, and acids containing methyl, ethyl, propyl, *iso*propyl, butyl, and amyl groups which were found not to give the alcoholic sodium hydroxide test.

† In the experiments with the different nitrites the liquid obtained in five or six experiments was collected and fractionated, and the alcohol, aldehyde, acid, and nitro-compounds were identified.

Conversion of Methyl Nitrite into Nitromethane.

The gaseous methyl nitrite was absorbed in well-cooled paraffin oil, and the solution obtained in this way was also cooled, during experiment, in ice, while a slow current of carbon dioxide was passed through it. Methyl nitrite being more volatile than the ethyl compound, a 20 per cent. solution was found convenient to use. The general behaviour of methyl nitrite is similar to that of ethyl nitrite. The conversion commenced at 100°, and at 120—130° oily drops of nitromethane collected. At a higher temperature formaldehyde and formic acid were obtained along with the nitro-compound, just as the corresponding aldehyde and acid were produced in the case of ethyl nitrite. Attempts were made to heat the nitrite dissolved in methyl alcohol in a sealed tube, but owing to the extreme volatility and inflammability of the methyl nitrite, the tube could not be sealed, even when cooled in a freezing mixture, as constant explosions took place.

Conversion of iso*Propyl Nitrite into β-Nitropropane.*

A 25 per cent. solution of *iso*propyl nitrite in paraffin oil was employed, the spiral condenser, inserted into the mouth of the flask, being two-thirds filled with water. The receiving U-tube was kept in water at 25—30°. At 100°, after four to five hours, a few minute drops of nitro-compound were obtained. At 125° the yield was greater, the best result being obtained at 125—130°. At higher temperatures the corresponding aldehyde and acid were produced, in addition to the nitro-compound. The quantity of available *iso*propyl alcohol being small, the platinichloride of the amine was not prepared.

Conversion of n*-Propyl Nitrite into Nitropropane.*

There was no necessity for using solutions of *n*-propyl nitrite in paraffin oil, as its boiling point is comparatively high, namely, 58—60°. On passing its vapour as usual through the tube, drops of nitro-compound collected at 125—130°. At a higher temperature the corresponding aldehyde was formed, and above 150° the acid was almost the main product.

The nitrite was also heated in a sealed tube in a furnace for five to six hours at 120°. After opening the tube, the liquid on fractionation yielded a fraction boiling at 126—128°, which, on reduction, furnished the corresponding amine. (Found, Pt = 36·61. Calc., Pt = 36·93 per cent.)

Conversion of iso*Butyl Nitrite into Nitro*iso*butane.*

*iso*Butyl nitrite, which boils at 70°, was passed through the heated tube, and also heated in a sealed tube. In the first case at 120—125° an oily liquid collected in the U-tube, which, in addition to the nitro-compound, contained butyl alcohol, butaldehyde, and butyric acid. At a higher temperature, the percentage of butyric acid becomes greater. The products from four experiments were mixed and fractionated. The fraction boiling at 130—135° was reduced to the corresponding amine and the platinichloride prepared. (Found, Pt = 34·87. Calc., Pt = 35·07 per cent.)

On heating the nitrite in a sealed tube at 125°, small quantities of the nitro-compound were obtained along with butyl alcohol and butyric acid, the alcohol forming the major portion.

Conversion of iso*Amyl Nitrite into* iso*Nitropentane.*

When amyl nitrite was heated under a reflux condenser to 120°, nitrous fumes slowly appeared, and at 150° they were evolved in larger quantities. When heated at 150—180° for six to eight hours, the liquid, on distillation, was found to contain very little nitrite, the greater part being amyl alcohol. The last fraction, however, responded to the test for nitro-paraffins.

On passing the vapour of *iso*amyl nitrite through the heated tube at 120° a liquid collected in the receiving tube, which responded to the test for nitro-paraffins. The liquid, however, contained alcohol and acid as well, the former preponderating. The fraction boiling at 138—147°, obtained by fractionation of the products of four experiments, was reduced to the corresponding amine, the platinichloride of which was analysed. (Found, Pt = 38·94. Calc., Pt = 39·23 per cent.)

It appears from the foregoing experiments that the production of aliphatic nitro-compounds is partly explained by the isomeric conversion of nitrites. In the preparation of nitro-compounds, either by the interaction of silver or mercurous nitrite and alkyl iodides or of alkyl sulphates and alkali nitrites, the substances are digested for many hours, and during the process of heating, even at 100°, partial conversion of nitrites into nitro-compounds would be possible, although in the case of gaseous nitrites like methyl and ethyl nitrites the formation of large quantities of nitromethane and nitroethane cannot possibly be due to isomeric conversion to a large extent. In the case of the preparation of the nitro-compounds, however, by heating mixtures of alkyl alkali sulphates and alkali nitrites, the alcohol formed by the decomposition of the alkyl sulphates or the aliphatic nitrites would dissolve large quantities of the aliphatic nitrites, which on prolonged digestion would be partly converted into the corresponding nitro-compounds.

Influence of Moisture on the Conversion.

In order to study the influence of moisture, the gaseous nitrite was dried by passage through one or two calcium chloride tubes and then passed into the heated tube, when it was found that very little liquid collected in the receiving U-tube and most of the nitrite was passing out unchanged. This phenomenon was observed in the case of all the nitrites. It appears that the presence of moisture, which is always present in the rapidly dried nitrites, facilitates the conversion of the nitrite into the nitro-compound.

In order to ascertain if the presence of larger quantities of moisture in the gaseous nitrites gives rise to a larger percentage of nitro-compounds, the nitrites were passed through a wash-bottle containing water before entering the heated tube. It was found that when surcharged with moisture the nitrite dissociated more rapidly, yielding larger quantities of alcohols, aldehydes, and acids without any appreciable increase in the yield of the nitro-compound. It appears that in the presence of traces of moisture, two reactions proceed simultaneously, namely, the conversion of the nitrite into nitro-compound and the dissociation of the nitrite; and with the increase in the proportion of water the latter reaction proceeds with greater rapidity.

Reduction of Aliphatic Nitrites to Amines.

Gaudion (*Ann. Chim. Phys.*, 1912, [viii], **25**, 125) observed that by passing a mixture of hydrogen and aliphatic nitrites over heated finely-divided nickel or copper, amines are obtained, but he was unable to explain definitely how amines could be produced by the reduction of nitrites. We have also obtained amines by passing a mixture of the nitrites and hydrogen through a heated tube containing reduced nickel.

The formation of small quantities of amines by the reduction of aliphatic nitrites can now readily be explained in view of the above experiments. It is the nitro-compounds that are actually formed which undergo reduction to amines, and not the nitrites themselves. Sabatier and Senderens (*Compt. rend.*, 1902, **135**, 225) have, as a matter of fact, shown that aliphatic nitro-compounds are thus reduced to amines by hydrogen in presence of heated nickel.

Theories of the Formation of Aliphatic Nitro-compounds.

The partial conversion of aliphatic nitrites into nitro-compounds has a theoretical bearing on the formation of nitro-compounds.

Neogi (T., 1914, **105**, 2371) has already shown that the theory of tautomerism cannot be applied to the aliphatic nitrites and nitro-compounds, as heavy atoms of silver and mercury as well as heavy alkyl radicles cannot be supposed to oscillate between an oxygen and a nitrogen atom, the true tautomerides being nitro-compounds and nitrolic acids. He therefore advanced two other hypotheses to account for the formation of nitro-compounds, namely, (1) isomeric conversion, and (2) formation of unstable additive compounds. The results of the present investigation show that the conversion of aliphatic nitrites into nitro-compounds takes place at a higher temperature, but, as the yield is very small, it alone is incapable of explaining the formation of the large quantities of nitro-compounds obtained by the interaction of silver or mercurous nitrite and alkyl iodides. The interaction of silver or mercurous nitrite and alkyl iodides is completed at 100°, whilst the conversion of aliphatic nitrites into nitro-compounds, although commencing at 100°, does not proceed to an appreciable extent below 120—130°. Moreover, ethyl and methyl nitrites, being gaseous, escape at the moment of formation, and have little chance of conversion into the nitro-compounds during digestion. In the case of the higher nitrites, however, especially when the interaction of alkyl sulphates and alkali nitrites takes place at a higher temperature, isomeric conversion would be partly responsible for the formation of the nitro-compounds.

The theory of isomeric conversion not being adequate to explain the formation of the entire quantity of the nitro-compound actually produced, the formation of unstable intermediate compounds becomes the only alternative explanation of the formation of the aliphatic nitro-compounds. This additive hypothesis is summarised thus: Nitrous acid, which forms aliphatic nitrites, and not nitro-compounds, with alcohols, evidently possesses the oxylic constitution HO·NO, and the inorganic nitrites, including silver and mercurous nitrites, being obtained simply by the neutralisation of nitrous acid with inorganic oxides, would also possess the same constitution. When the alkyl iodides react with silver or mercurous nitrite, or when the alkyl sulphates react with alkali nitrites, two reactions take place, namely, (1) the aliphatic nitrites are obtained by direct interchange, and (2) unstable intermediate compounds are formed, which decompose with the formation of nitro-compounds, thus:

$$AgO{\cdot}N{:}O + C_2H_5I = AgO{\cdot}N(C_2H_5){\cdot}OI = C_2H_5{\cdot}NO_2 + AgI.$$
$$KO{\cdot}N{:}O + C_2H_5KSO_4 = KO{\cdot}N(C_2H_5){\cdot}OKSO_4 = C_2H_5{\cdot}NO_2 + K_2SO_4.$$

The relative proportions in which the nitro-compounds would be produced would depend on the extent to which the intermediate compounds are formed. As the nitrites and nitro-compounds are formed in many cases in almost equal quantities, the two reactions proceed in those cases to an almost equal extent. To the reactions thus indicated is to be added the effect of the partial conversion of the nitrites into nitro-compounds where the digestion takes place at a higher temperature. In the case of nitrous acid the intermediate compounds not being formed, no nitro-compounds are obtained.

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