XCIV.—*The Action of Nitrogen Trioxide and Tetraoxide on Alcohols. Part I.*

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IN attempting to prepare benzylic nitrite, a substance which appears not to have been obtained, we tried, among other methods, the action of a chloroform solution of nitrogen trioxide on benzylic alcohol, anticipating the following reaction :

On adding the deep blue solution of the trioxide to the alcohol, the blue colour changed at once to a light brown, and the liquid became turbid from the separation of minute drops of water. A result of this kind would occur supposing the above reaction to have taken place ;

but, on standing, the liquid became green, probably from the presence of free nitrogen trioxide. The test-tube in which the reaction was tried was placed on one side for a day or two, and on returning to the experiment, the chloroform had evaporated, and the liquid which remained smelt strongly of benzaldehyde. It gave a copious precipitate with phenylhydrazine, which had the correct melting point (153°) for the hydrazone of benzaldehyde. The reaction was repeated with the same result, and it was found that aldehydes were produced in the same manner, although much less abundantly, from methylic, ethylic, propylic, and amylic alcohols, and from ortho- and para-nitrobenzylic alcohols.

If, after the addition of the nitrogen trioxide solution to benzylic alcohol, the product is immediately poured into caustic soda solution, so that the reaction is stopped, only a very small quantity of benzaldehyde is formed. That the formation of aldehyde is a gradual one is further evident from the following experiments.

The strength of the nitrogen trioxide solution was roughly determined, to begin with, by pouring 5 c.c. into 100 c.c. of dilute caustic soda solution cooled in ice and shaken until the chloroform was colourless. Ten c.c. of the alkaline liquid was withdrawn, diluted largely with water, acidified with sulphuric acid, and titrated with standard permanganate solution.

It was found in this way that 5 c.c. of the chloroform solution contained rather over one equivalent of trioxide corresponding to 1 gram of benzylic alcohol.

Into four glass tubes, with constrictions for sealing, 1 gram of benzylic alcohol was introduced, and 5, 8, 10, and 15 c.c. respectively of trioxide solution, corresponding to 1, $1\frac{1}{2}$, 2, and 3 molecules of trioxide, were added. These tubes were then sealed up and allowed to stand. After 3 days, the tubes with 5 and 10 c.c. of trioxide solution were opened, poured into caustic soda solution, and the trioxide titrated as above described. The chloroform solution was then withdrawn and the alkaline liquid repeatedly extracted with chloroform. The combined chloroform solution and washings were dehydrated over calcium chloride, the chloroform distilled off, and the aldehyde in the residue estimated as the phenylhydrazone as follows. The contents of the distilling vessel, which was rinsed out with alcohol, were poured into water, and 1 gram of phenylhydrazine dissolved in excess of dilute acetic acid was added. After standing for a short time, the phenylhydrazone was filtered, dried at 100° , and weighed. After 4 days, the tubes with 8 and 15 c.c. of trioxide were opened and treated in the same manner. The following are the results obtained :

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No. of experiment.	Weight of benzylic alcohol in grams.	Volume of N_2O_3 solution in c.c.	Time in days.	Weight of hydrazone in grams.	Excess of N_2O_3 left in grams.
1	1	5	} 3	1	0.069
2	1	10		1.04	spoilt
3	1	8	} 4	1.21	0.46
4	1	15		1.21	0.93

A fifth experiment was afterwards made with 10 c.c. of the trioxide solution, which had been frequently exposed to the air and had a greenish tint. After standing 5 days, the quantity of phenylhydrazone amounted to 1.33 grams. This experiment will be referred to again.

Two conclusions may be drawn from these experiments: firstly, time is a factor in the formation of benzaldehyde; and secondly, the reaction occurs between equivalent molecules of benzylic alcohol and nitrogen trioxide.

It is not easy to formulate the reaction. The simple equation which explains the immediate separation of water on adding the two substances, which may be expressed as follows:

is obviously untenable, as it neither accounts for the slow formation of the aldehyde nor the production of the green trioxide on standing. The correct interpretation of the reaction follows from the study of the action of nitrogen tetroxide on benzylic alcohol, to which we next turned our attention.

In the fifth experiment referred to above, on estimating the quantity of trioxide remaining, we were surprised to find that it was nearly equal to the quantity in the original trioxide solution. This could only be explained by supposing that the excess was due to the reduction of some tetroxide in the original solution to trioxide. That a considerable quantity of tetroxide was present was evident from the green colour of the solution, as well as from the fact that during the frequent removal of the stopper in the previous experiments, a quantity of air must have entered.

In order to determine the action of nitrogen tetroxide on benzylic alcohol, a quantity of dry tetroxide was prepared.* On adding a few

* A very simple method for preparing fairly large quantities of pure nitrogen tetroxide is first to make the trioxide in the ordinary way by the action of concentrated nitric acid (sp. gr. 1.4) on arsenious oxide, and then to pass the gas through a Woulfe's bottle cooled in ice. To the exit tubulus of the Woulfe's bottle, a T-piece is attached, through the horizontal arm of which a stream of oxygen can be passed. Although the liquid trioxide is practically unacted on by oxygen, rapid combination takes place between the oxygen and the gaseous trioxide. After

drops to a few drops of benzylic alcohol, a violent reaction occurred, the liquid began to boil, and after standing, a quantity of benzaldehyde was found to have been produced.

On diluting the tetroxide with chloroform and adding the solution to the alcohol kept cool in water, the action was moderated and the following characteristic changes were observed. A clear, light brown liquid is first produced, which quickly becomes turbid, this being due, as in the case of the trioxide, to the formation of drops of water. At the same time, the brown liquid begins to change colour and becomes a more and more intense green on standing. An experiment made with 1 gram of benzylic alcohol and 1 molecular equivalent of tetroxide gave at the end of 5 hours 1.36 gram of phenylhydrazone. The strength of the tetroxide solution was determined, as previously described for the trioxide, by pouring a measured volume into an ice-cold solution of caustic soda and titrating the amount of trioxide present, from which the quantity of tetroxide can be calculated according to the equation

In order to determine whether the benzaldehyde was formed at once on the addition of the tetroxide, or slowly as in the case of the trioxide, a second experiment was made. After mixing molecular equivalents of alcohol and tetroxide, the mixture was poured into dilute caustic soda solution. The chloroform solution now contained only a trace of benzaldehyde. The nitrite solution, on the other hand, required almost exactly the same quantity of permanganate as the original tetroxide solution. The latter result is curious, because if the two reactions are expressed as follows :

one would expect that the splitting off of water in the second equation would produce a double quantity of trioxide. The question then arises, What has become of the missing molecule of trioxide in the second equation?

The idea naturally suggested itself that it had remained attached to the benzylic alcohol molecule.

passing through two U-tubes containing anhydrous calcium nitrate, the tetroxide can be collected in a distilling flask cooled in a freezing mixture. The nitrogen tetroxide is then redistilled by attaching a condenser and receiver and surrounding the distilling flask with warm water. This distillation is necessary, as a small liquid residue always remains, which is probably derived from the decomposition of the cork. By this method, over 100 grams of dry tetroxide free from trioxide have been prepared in half a day.

In order to verify this, equivalent molecules of benzylic alcohol and nitrogen tetroxide in chloroform were mixed and immediately poured on to ice. The liquid was then carefully neutralised with a 5 per cent. caustic soda solution, when the chloroform remained of a pale yellow colour. The chloroform solution was then separated, dehydrated over calcium chloride, and the chloroform distilled off on the water bath. An amber-coloured liquid remained behind, and it contained nitrogen. The liquid was alternately heated for a few minutes on the water bath and placed in a vacuum desiccator over olive oil to remove traces of chloroform. These operations must be rapidly performed, as the liquid is very unstable, slowly evolving nitrous fumes at the ordinary temperature and forming benzaldehyde.

The following results were obtained on analysis from two different preparations. The numbers are low for the reasons stated:

0.2035 gave 14.8 c.c. moist nitrogen at 21° and 751 mm. $N = 8.6$.

0.1823 „ 13.65 „ „ „ at $18\frac{1}{2}^{\circ}$ „ 760 mm. $N = 8.7$.

$C_7H_7NO_3$ requires $N = 9.1$ per cent.

The liquid has a yellow colour, and a sweet, penetrating smell. As already mentioned, it decomposes on standing; on heating, the decomposition is more rapid, and, on boiling, it immediately darkens in colour. It gives a characteristic reaction with strong hydrochloric acid. On the addition of the acid, it becomes a deep red colour, and, on heating, a rapid effervescence and evolution of nitrous fumes occurs, accompanied by the disappearance of the red colour. The liquid is now wholly converted into benzaldehyde.

This was shown by extracting the product with ether and shaking up with sodium bisulphite solution, when the bisulphite compound was formed, and, after separating and distilling the ether, no residue was left. The benzaldehyde was also converted into the phenylhydrazone, m. p. 153° . On oxidation with chromic acid mixture, the compound is converted into benzoic acid, identified by its melting point (120°) and by its characteristic smell.

On reduction with the aluminium-mercury couple (Trans., 1890, 57, 811) in alcoholic solution containing hydrochloric acid, the substance is decomposed into benzylic alcohol, benzylamine, and ammonia; no hydroxylamine was formed. After reduction, the alcohol was distilled off, and ether added to the residue. The benzylic alcohol dissolves, and a mixture of benzylamine and ammonium hydrochloride remains and was separated from the benzylic alcohol by filtration.

The benzylic alcohol was identified by its boiling point (206°) and by the boiling point of its benzoate (320°).

The mixed hydrochlorides of benzylamine and ammonia were treated with a strong solution of caustic soda and extracted with ether.

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The benzylamine dissolves in the ether, from which it may be separated by distilling off the ether. The residue thus obtained was dissolved in dilute hydrochloric acid, and platinic chloride added, when the yellow, crystalline platinum salt was formed. An analysis of the platinum salt gave the following result :

0.1131 gave 0.0358 platinum. Pt = 31.6 per cent.

$(C_6H_7N)_2H_2PtCl_6$ requires Pt = 31.4 per cent.

The compound was further identified by the solubility in water of the hydrochloride and by its m. p. 247—250°, and by the solubility of the free base in water, alcohol, and ether, and its insolubility in strong caustic soda solution.

From the character of the various reactions which have been described, we are disposed to assign provisionally the following constitution to the compound, which may be called phenylnitrocarbinol,

At the same time, we admit that the evidence is still incomplete. Assuming this formula, we may proceed to explain the interaction of benzylic alcohol and nitrogen tetroxide.

In the first stage of the reaction corresponding to the separation of water and the turbid appearance of the liquid, a product which may be termed benzylidene nitrosate is formed, as follows :

The existence of a compound of this constitution, although we have not succeeded in isolating it, seems probable in view of the recent researches of Scholl (*Ber.*, 1888, 21, 509 ; 1890, 23, 3490 ; 1895, 28, 1361) and of Fileti and Ponzio (*J. prakt. Chem.*, 1895, [ii], 51, 498, and 1897, [ii], 55, 186), who have isolated compounds of the general formula $R \cdot C(N_2O_4) \cdot R$ and $R \cdot C(N_2O_4) \cdot CO \cdot R$ by the action of nitrogen tetroxide on ketoximes and isonitrosoketones, and by the action of nitric acid on ketones. Benzylidene nitrosate gradually loses nitrogen trioxide on standing and forms benzaldehyde, thus :

This will account for the fact that the solution assumes a deep green colour on standing and also that the quantity of trioxide increases *pari passu* with that of the benzaldehyde. If, on the other hand, the nitrosate is poured into water it is hydrolysed and phenylnitrocarbinol is formed together with nitrous acid,

The substance, which we term phenylnitrocarbinol, is probably identical

with the compound first investigated by Lippmann and Hawliczek in 1876 (*Ber.*, 9, 1463) to which they gave the name of nitrobenzoyl. The latter substance was obtained as a bye-product in the preparation of metanitrobenzaldehyde by the action of a mixture of concentrated nitric and sulphuric acids on benzaldehyde. Although the authors assign the formula $C_7H_5NO_3$ to the compound, we are disposed to think from the few properties which are described that it is identical with the compound we have obtained. Thus, like our compound, it is a yellow liquid, which decomposes on boiling and yields benzoic acid on oxidation with chromic acid mixture.

In order to compare the two substances, we attempted to prepare Lippmann's compound by the method he describes. The specified quantities of acid and benzaldehyde were mixed together, and the product after dilution with water was extracted with ether, in which both the nitrobenzaldehyde and the nitrobenzoyl are soluble. The ethereal solution was shaken up with sodium bisulphite solution and allowed to stand. The nitrobenzoyl does not combine with sodium bisulphite, but remains dissolved in the ether. The ether was therefore decanted and distilled, when the nitrobenzoyl should remain behind as a light yellow oil. In our experiments, a very small quantity of oil remained, but in a short time it solidified, forming a mass of colourless crystals, which, after recrystallisation from water, melted at $131-133^\circ$. This substance is apparently an acid, for it dissolves readily in caustic soda solution, but it was not further investigated.

It is evident that the conditions under which our experiment was conducted differed in some essential point from those of Lippmann and Hawliczek, and as we were unsuccessful in preparing their compound, a direct comparison of the two substances had to be relinquished.

Supposing Lippmann's compound to have the composition we have assigned to it, it is easy to formulate a theory as to its formation. By the action of nitric acid on benzaldehyde, some benzoic acid is probably formed, and, at the same time, some nitric acid is reduced to lower oxides of nitrogen. Nitrogen trioxide, if present, might combine with the benzaldehyde to form the nitrosate we have described, which would be decomposed by water, yielding phenylnitrocarbinol.

Unfortunately for the theory, nitrogen trioxide does not combine directly with benzaldehyde. The action was tried with a solution of the trioxide in chloroform and with pure nitrogen trioxide at the ordinary temperature and at the freezing point, and in the presence of strong sulphuric acid. This result is perhaps not surprising, when one considers how readily the nitrosate parts with nitrogen trioxide and forms benzaldehyde. It is possible that the trioxide in the nascent state may act otherwise, but, however this may be, we have failed to bring about the combination.

It now remains to explain the interaction of nitrogen trioxide and benzylic alcohol. It is probably similar to that of nitrogen tetroxide and the alcohol, as the same series of changes are observed. Thus a nitrosite may be formed in the first stage, as follows :

This would account for the disappearance of the blue colour and the formation of water. The nitrosite, like the nitrosate, will slowly decompose on standing, giving rise to nitric oxide and benzaldehyde,

If there is any tetroxide in the trioxide solution or any oxygen in the vessel in which the reaction occurs (both of which were invariably present), a sufficient quantity of trioxide will be formed to impart a green colour to the liquid ; but the reaction will take place between equal molecules of alcohol and nitrogen trioxide, and so much trioxide will at once disappear from the liquid, which agrees with the experimental results given at the beginning of the paper. This view requires further experimental confirmation, which we hope to bring forward in a future communication.

We have tried the action of nitrogen tetroxide on various other alcohols and also on hydroxyl compounds (oxy-acids, &c.), with results upon which we are at present engaged. In conclusion, we desire to thank Mr. J. H. Sugden, B.Sc., for substantial help in the early part of this investigation.