

XVIII.—*On Nitro-compounds.* (Part I).

By EDMUND J. MILLS, B.Sc., F.C.S.

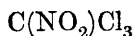
THE large and important group of substances known as “nitro-compounds” has always been admitted to a considerable share of the attention of chemists. The ease with which these bodies can be formed and reduced, the varied products to which they give rise on reduction, their critical value in the establishment of rational formulæ, are circumstances which may well account for the interest felt in them both by the purely scientific and the commercial experimenter. It has, accordingly, been to me a

matter of some surprise that they have not hitherto been submitted to a systematic investigation, either with the view of classifying them in a satisfactory manner, or of solving some of the very obscure but attractive problems which they present.

The following paper contains a detailed account of some experiments still in progress, in which I have endeavoured to bear both the above objects in mind. As a means of obtaining results capable of being used as a basis of classification, no method held out better promise than that of reduction—a process, indeed, to which the majority of nitro-compounds had been already submitted. But, since the labours of chemists had not been directed by an intention similar to the present, and had shown that a change of the reducing agents, or a difference in the mode of applying a single one, has a material influence on the product of the reaction, I determined to acquire new data by acting on a number of typical nitro-compounds with one reducing agent, taking care to keep the circumstances of the reduction as uniform as possible. For this purpose I have selected hydriodic acid—a reagent which, in the hands of Lautemann and others, has become so distinguished in value and interest. We owe to Gay-Lussac* the examination into its action on nitric acid, and to Lautemann† the recent inquiry into its behaviour with picric acid. The liquid and solid compounds thus treated are as follow :

1. *Chloropicrin.*

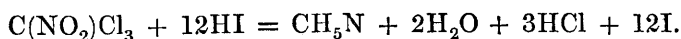
This substance, the discovery of Stenhouse, and having the well-known formula—



was observed by Geisse‡ to yield methylamine when submitted to Béchamp's process. He thus expresses the reaction :—



It was natural to expect a similar result from the employment of hydriodic acid—



* Gmelin's Handbook, Watts's translation. Vol. ii., pp. 263, 396.

† Ann. Ch. Pharm. cxxv. 1.

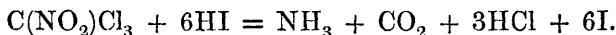
‡ Ann. Ch. Pharm. cix. 282.

Accordingly chloropicrin (the purity of which had been ascertained by a chlorine determination) was sealed up with fuming hydriodic acid. A very slight alteration was apparent, even in the cold, on standing several days; but when digested in the water-bath for four-and-twenty hours, it was evident that the contents of the tubes had undergone a powerful reaction. On cooling, iodine crystallised out in abundance. There was a slight report on opening the tubes; the liquid they contained, separated from the free iodine, to a great extent, by filtration, furnished, on evaporation to dryness, crystals of hydriodate of *ammonia*. After twice recrystallising, the purity of the latter substance was ascertained by an iodine determination.

0.30275 grm. substance, dried over oil of vitriol, furnished 0.4918 grm. iodide of silver.

	In 100 parts.	
	Experiment.	Theory.
Iodine	87.86	87.58

The crystals contained no methylamine. Geisse, on the other hand, obtained a product perfectly free from ammonia. The reaction may be thus written—



Besides qualitatively verifying this, I have determined the amount of ammonia produced.

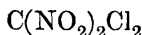
0.6795 grm. substance, after treatment as above, and conversion of the ammonia into platinum-salt in the usual manner, gave 0.4008 grm. platinum, corresponding to 10.13 per cent. of ammonia.

Experiment.	Theory.
10.13	10.33

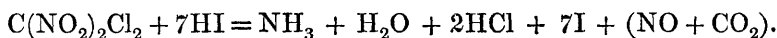
I attempted a quantitative determination of this kind, but without success, by heating the mixture in an oil-bath to 125°C. The operation was very soon terminated. Small white crystalline plates were visible at the top of the tube. They were readily soluble in alcohol, and probably consist of chloride of carbon. A temperature of 100°C. seems the most advantageous for the proper performance of the reaction.

2. *Marignac's Oil.*

This compound, known also as the chloride of dinitromethylene, which not only by the formula



but also in type and character, is most closely connected with the preceding, was next submitted to treatment. It had been prepared by my friend, Mr. Walter Stewart, in accordance with Marignac's directions, and its purity was ascertained as in the previous case. A quantity of the oil was placed, together with some hydriodic acid, in a stout tube, through which a slow and constant current of carbonic anhydride was kept passing. The tube was surrounded with water, which could be gradually heated, and the gas proceeding from it was conducted, by means of a cork and an evolution-tube, into an upright glass cylinder (filled partly with potash-solution and partly with mercury) placed over a pneumatic trough. The sp. gr. of the hydriodic acid used, was about 1.58. The attack, as indicated by the elimination of free iodine, appeared to commence at nearly 60° C., but unabsorbed gas was not given off till the temperature of the bath was 94° C. This seems to indicate an intermediate stage in the reaction, which I may at once express thus—



Into the cylinder containing the unabsorbed gas, excess of oxygen was first introduced (when great absorption took place), and subsequently pyrogallic acid. In every operation there was a variable quantity of residual gas, very readily soluble in water, and consisting of nitrous oxide. In this respect, therefore, hydriodic acid resembles hydrosulphuric acid; for there can hardly be any doubt that nitric oxide is first eliminated and then reduced partially. The amount of ammonia produced was ascertained as in (1).

0.69550 grm. substance furnished 0.38725 grm. platinum = 9.59 ammonia per cent.

Experiment.
9.59

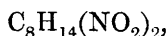
Theory.
9.71

The other products of the reaction were only qualitatively de-

terminated. Very many attempts, with this and other nitro-compounds, to determine the free iodine when nitric oxide has been evolved, have convinced me that in such a case the method of Bunsen is inapplicable.

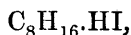
3. *Dinitro-octylene.*

If, as Kekulé has done,* we view the compounds just discussed as more immediately connected with marsh-gas, it becomes interesting to inquire in what manner a nitro-derivative directly obtained from an olefiant, will behave with hydriodic acid. Accordingly, I have availed myself of dinitro-octylene, one of the important products obtained by Bouis,† when investigating the nature of castor-oil. The octylene was prepared by the action of chloride of zinc on octylic alcohol, and its derivative



by the treatment of the former with a mixture of sulphuric and nitric acids, and subsequent washing with distilled water.

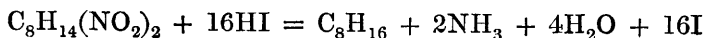
A mixture of dinitro-octylene and hydriodic acid of sp. gr. 1·50, becomes homogeneous on shaking, and blackens, with formation of octylene and ammonia, below 100° C. At the same time a heavy oil is produced, probably consisting of the compound



and this sometimes to so great an extent that the characteristic odour of the olefiant is not perceptible. It is necessary to use the freshly-prepared substance in this experiment; for the nitro-compound, if long kept, becomes altered, with the formation of certain products of a most rancid odour, which, on heating with hydriodic acid, evolve small quantities of nitric oxide.

I have only to add that, in preparing the dinitro-octylene, I have noticed, in small quantity, the white, crystalline body mentioned by Bouis.—For treatment, the substance was dried for a fortnight over oil of vitriol.

0·56175 gram. substance, heated with hydriodic acid, in a sealed tube, for a few hours to 100° C., gave 0·57155 gram. platinum = 17·47 per cent. ammonia. The equation



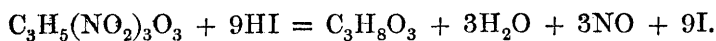
* Ann. Ch. Pharm. ci. 204 (1857).

† Ann. Ch. Phys. [3] xliv. 77.

requires 16·83 per cent.

4. *α-Trinitro-glycerin.*

Desirous of witnessing the behaviour of an alcohol-derivative with hydriodic acid, I prepared trinitro-glycerin* for this purpose. Heated with the acid (of the sp. gr. last-mentioned) to a point which I was unable accurately to fix, but which lay considerably below 90° C., trinitro-glycerin is decomposed with great rapidity, yielding glycerin and nitric oxide, but no ammonia. The nitric oxide evolved is tolerably free from nitrous oxide:



5. *Nitro-benzol.*

It was impossible to omit the aromatic analogue of marsh gas from this list. Perfectly pure nitro-benzol, long heated to 100° C., with ordinary weak hydriodic acid, suffers no change. But I have ascertained that when it is heated with six times its volume of hydriodic acid of sp. gr. 1·44, in a tube 13·3 mm. in diameter, with frequent agitation, complete opacity of the hydriodic acid takes place at 104° C. The product of the reaction is aniline in the state of hydriodate, perfectly free from the ammonia which is not unfrequently liberated in the application of Béchamp's process (Scheurer-Kestner). The aniline-salt thus obtained seemed to differ in no respect from that which arises in the contact of common aniline with hydriodic acid. It yielded, moreover, the following result on analysis:

0·2900 grm. substance, dried over sulphuric acid, gave 0·3093 grm. iodide of silver, = 57·64 per cent. iodine.

Experiment.	Theory.
57·64	57·47

6. *Hexnitro-mannite.*

This substance may be taken as the best defined of those highly

* Professor Church, some time since, communicated to me a fact which he had observed—that trinitro-glycerin gradually loses its well-known explosive properties, the loss being accompanied with the formation of oxalic acid. I have verified this observation, which will be more closely examined hereafter. Meanwhile, the new compound may be termed *β*-trinitro-glycerin, and the explosive variety, *α*-trinitro-glycerin.

replaced compounds which are obtained by treating the members of the saccharine group with a mixture of sulphuric and nitric acid. It was prepared and purified in the usual manner. Treated with strong fuming hydriodic acid, hexnitro-mannite is readily attacked, with evolution of heat and nitrous fumes. The temperature, in two experiments, rose from 22° C. to 30° C. When heated in a water-bath to 81° C., with hydriodic acid of sp. gr. 1·603 at 17° C., as mentioned in (2), the latter became opaque; at a somewhat higher temperature, the development of nitric oxide took place with great regularity. The gas was contaminated with a small quantity of nitrous oxide. The deep brown liquid obtained when the reaction had terminated was boiled for some time with carbonate of lead, in order to volatilise the free iodine and convert the remaining hydriodic acid into iodide of lead. The solution was cooled, filtered, evaporated to dryness on the water-bath and extracted with hot alcohol, whence regenerated mannite* separated on cooling. I was unable to notice any difference between the mannite thus obtained, and that which had not been submitted to nitration. Twice crystallised, and dried at 100° C., it gave the following result on combustion :

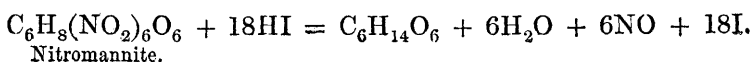
0·3734 grm. substance, furnished 0·5354 grm. carbonic anhydride and 0·2629 grm. water.

Theory.			Experiment.
C ₆	= 72	39·56	39·11
H ₁₄	= 14	7·69	7·82
O ₆	= 96	52·75	—
	<hr/>	<hr/>	
	182	100·00	

In this reduction no ammonia is produced, but I have found that there is a small quantity of a secondary body found, which becomes brown on exposure to a heat 100° C. Other experimenters, also, when investigating nitro-compounds of this class, have observed that more than one reaction takes place when they have submitted them to reduction. The following equation,

* The regeneration of mannite from its nitro-compound was effected by Dessaignes (Compt. rend. xxxiii. 462) by means of sulphide of ammonium; the nitro-compounds of melampyrin, cellulose, and erythromannite have been reduced, in like manner, by Eichler, Béchamp, and Stenhouse respectively.

therefore, though representing a part of what takes place, does not, strictly speaking, include the whole :



7. Nitraniline.

The two modifications of this substance, known as α and β nitraniline, the discoveries of Hofmann and Muspratt,* and of Arppe† respectively, have long been distinguished as furnishing one of the most remarkable cases of isomerism we possess. Accordingly, I have subjected them to the action of hydriodic acid, with the view of ascertaining whether the employment of this reagent would assist in solving this long-investigated problem.—The α -nitraniline was prepared by the action of sulphide of ammonium on dinitro-benzol; the β -nitraniline by the action of potash on nitro-acetanilide‡. Both substances were dried at $100^\circ\text{C}.$, and analysed.

α -nitraniline. 0.2865 grm. substance gave 0.5477 carbonic anhydride and 0.1179 grm. water.

β -nitraniline. 0.51575 grm. substance gave 0.98725 grm. carbonic anhydride and 0.21450 grm. water.

Theory.		Experiment.	
		α	β
$\text{C}_6 =$	72	52.14	52.39
$\text{H}_6 -$	6	4.57	4.62
$\text{N}_2 =$	28	—	—
$\text{O}_2 =$	32	—	—
	<hr/> 138		
	<hr/> 100.00		

The fusion-points were also taken, and compared with those obtained by other observers :

	α	β
Hofmann and Muspratt	$110^\circ\text{C}.$	—
Arppe	108°	141°
Mills.....	$110^\circ.5$	$142^\circ.2$

* Ann. Ch. Pharm. lvii, 201.

† Ann. Ch. Pharm. xc, 147.

‡ Hofmann, Ann. Ch. Pharm. cxxi, 281

Either of these substances, when boiled with hydriodic acid of various strengths, gave rise to a separation of free iodine and the hydriodate of a base, doubtless the corresponding phenylenediamine.* The hydriodates are splendid salts, probably colourless when pure, and differing in a marked manner in their solubility in hydriodic acid, the β -hydriodate being very little soluble, while the α -hydriodate dissolves with ease. The β -hydriodate crystallises in broad, flat rectangular plates, with the lustre of mica; the α -hydriodate in small plates, not so well defined or beautiful as those of the β -salt. It appeared to be of considerable interest to ascertain whether the two nitranilines were attacked at the same or different temperatures. The hydriodic acid employed had been heated, either with phosphorus or zinc-amalgam, and distilled not long before the experiment. The substance, dried at 100°C ., was weighed in a tube of small dimensions, which was introduced into a wide test-tube of about 1.5 times its diameter, and 5 c. c. of hydriodic acid were then added. A thermometer was inserted into the liquid, and supported by a cork (pierced with an additional aperture), so as to occupy the axis of the large tube. The temperature at which the cylindrical portion of the mercury in the bulb ceases to be visible was carefully noted.† I term this, for convenience sake, the "*attack-point*." In taking a pair of observations, it is necessary that the observer's eye, the centre of the apparatus, and some fixed object, should be in the same straight line in each case. I have used the same apparatus in every experiment, and find that accuracy is easily obtained with a little practice. On contact with hydriodic acid, β -nitraniline usually dissolves in the cold, while α -nitraniline requires moderate heating to effect its solution.

All the circumstances of the experiments being otherwise alike, the only source of error appears to be the presence of free iodine, which, existing even to a very small extent in the hydriodic acid used, appears to lower both attack-points,—that of the β -nitraniline points more especially; which, indeed, is in accordance with the observation of Hofmann,‡ that the base obtained from this substance, in presence of an oxidising agent, produces violet and

* Hofmann, *Compt. rend.* lvi, 21.

† A bath of oil of vitriol, the upper surface of which was level with the hydriodic acid, was employed in each experiment.

‡ *Loc. cit.*

blue colouring matters with great facility. Hence, in the results mentioned below, the attack-point of β -nitraniline is probably in every case under the truth. Indeed, on two occasions I have in this way obtained altogether opposite results.

The following are selected from a considerable number of experiments:—

Internal Diameter of Tube, 16·51 m.m.
Hydriodic Acid used, 5 c.c.

Weight of Substance.	Sp. gr. of HI.	α -attack.	β -attack.	Difference.
0·25 grm.	1·441	94°·4 C.	98°·3 C.	3°·9 C.
0·25 "	1·449	93°·3	97°·2	3°·9
0·30 "	1·462	93°·9	96°·6	2°·7
0·30 "	1·529	82°·8	93°·9	11°·1
0·30 "	1·603	81°·7	92°·8	11°·1

Hence β -nitraniline is attacked at a higher temperature, and consequently with greater difficulty than α -nitraniline. The weaker the acid, the higher is the attack-point; with very strong acid I have found they are identical, or rather undistinguishable, as might have been expected. A range of weight in the substance employed of 0·15 grm. to 0·30 grm. makes no difference in the attack-point.

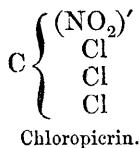
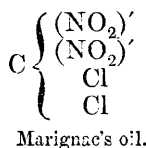
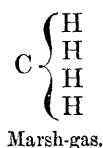
It may be safely asserted that any nitro-compound, when mixed with hydriodic acid of sp. gr. 1·7, and heated to 100° C., is decomposed, with the conversion of its nitryl (NO_2)' into (NH_2)', or else into (NO)'. Using for the last two groups the names "amide" and "nitrosyl" respectively, we may arrange nitro-compounds in two leading divisions *according to their products of reduction*, viz., "Amido-gens," and "Nitroso-gens," with an intermediate group of "Amido-nitroso-gens." The substances discussed in the above paper will then be arranged as follows;

<i>Amidogens.</i>	<i>Amido-nitrosogens.</i>	<i>Nitrosogens.</i>
Chloropicrin.	Marignac's oil.	Nitric acid.
Dinitro-octylene.		{ α -Trinitroglycerin.
Nitrobenzol.		{ β -Trinitroglycerin ?
{ α -nitraniline.		Hexnitro-mannite.
{ β -nitraniline.		

a list which, from the representative nature of the bodies it contains, might, without doubt, be very considerably extended in each

of its divisions. It is so easy to decide, in most cases, to which class a given nitro-compound belongs, that a few minutes' examination only need be now necessary to ascertain whether it will yield a base or otherwise.

On comparing together the reactions described in (1) and (2), it is to be noticed what a striking difference is presented by two bodies precisely similar in type, and remarkably like each other in all their physical properties.



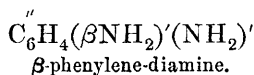
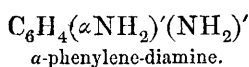
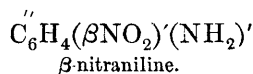
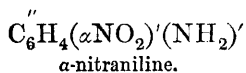
Only one equivalent of nitryl in Marignac's oil behaves like the single equivalent contained in chloropicrin. Hence there must be two isomeric forms of nitryl,* the one yielding nitrosyl, the other amide, when reduced as I have indicated.

If nitro-benzol be converted into aniline, then into acetanilide, nitro-acetanilide, and lastly nitraniline, we perceive that the phenyl-residue $(\text{C}_6\text{H}_4)''$ is the same, formally, throughout these changes. Again, if some of the same nitro-benzol be converted into dinitro-benzol, and this into nitraniline, we see still that the phenyl-residue is unaltered. Moreover, since we have not yet an isomer of aniline, or, at any rate, one which affects the present argument, it follows that these isomeric aniline-derivatives are not to be accounted for by the existence in them of two kinds of amide $(\text{NH}_2)'$. We are, therefore, forced to the conclusion that, in the two nitranilines, we have two kinds of nitryl present. In the circumstance of attack-point this reasoning is experimentally established. The only substances to which the elimination of iodine can there be due, are, nitryl and hydriodic acid; but, as the hydriodic acid is the same in both cases, it follows that the dual nature of nitryl must be the cause of the isomerism. I have no doubt that the two kinds of dinitro-phenyl obtained by Fittigt† are also to be accounted for in this manner, and I consider that α - and β -phenylene-diamine contain amide of two kinds, derived

* Mills, Chem. News (1863), No. 183. Two forms *poly*-meric with each other are believed to exist by Playfair and Wanklyn. (Trans. Roy. Soc. Edin. xxii, 462.)

† Ann. Ch. Pharm. cxxiv, 285.

from the two kinds of nitryl. The following are some of the formulæ I have adopted :—



When we reflect that isomeric phenyl-compounds, with scarcely an exception, contain nitrogen, we may expect to find the dual nature of nitryl, ere long, producing results of very wide application. Meanwhile I am continuing this examination, and am in hopes of obtaining a compound of nitryl, analogous to chloride of acetyl, whose nitryl may be thus transferred to a hydrocarbon unchanged; in this manner I trust to be able to fix the kind of nitryl that may be present in any nitro-compound.

I desire to express my best thanks to Professor Anderson for the use of his laboratory.
