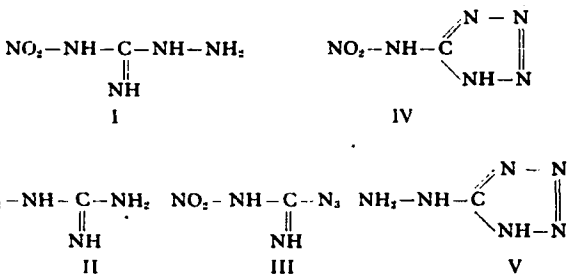
DIAZOTIZATION OF NITROAMINOGUANIDINE

By T. E. O'CONNOR, G. FLEMING, and J. REILLY

Nitroaminoguanidine on diazotization yields nitroguanidine and nitroguanyl-azide which may be isomerized to 5-nitramine-tetrazole. Nitroguanyl azide acts as a dibasic acid when titrated with alkalis, as it is quantitatively isomerized to the dibasic nitramine-tetrazole. Volumetric procedures for the estimation of the azide and its isomer are described.

Nitroaminoguanidine (I) was first prepared by Phillips and Williams[1] by the hydrazinolysis of nitroguanidine (II). Its heavy-metal salts have found application as explosive components[2, 3] while American workers[4, 5, 6] have utilized it for characterizing carbonyl compounds as nitroguanyl-hydrazones.

The present investigation of its interaction with nitrous acid was undertaken to provide a comparison with the diazotization of aminoguanidine, which has been the subject of intensive investigation.[7]



I IV

II III V

Nitroaminoguanidine has been found to interact readily with nitrous acid to yield nitroguanidine and a compound of empirical formula $CN_6H_2O_2$ to which we assign the structure (III); *nitroguanyl azide*. The azide structure of this compound is suggested by its liberation of nitrogen on boiling with acids, its interaction with hydriodic acid, when, in addition to nitrogen, it liberates one mole of iodine, but more especially by its facile cyclization to the isomeric tetrazole.

This isomerization, which is a general reaction of imino-azides, yields a compound which differs profoundly from the parent azide. *5-Nitramine-tetrazole* (IV), which has not previously been described, is best obtained in the form of its disodium salt by refluxing the azide solution with two equivalents of sodium acetate. Besides sodium acetate, alkalis or ammonium hydroxide are effective isomerizing agents.

To establish the structure of nitramine-tetrazole, it was reduced to 5-hydrazino-tetrazole (V), the benzylidene derivative of which has been characterized by Thiele.[8]

The interaction of nitroguanyl azide with dilute alkalis is unexpected. Solutions of the azide may be titrated in the presence of phenolphthalein with alkalis. A sharp end-point to the titration is readily obtained but equivalent determinations, based on such titrations, yield a value of approximately 65 instead of an expected 130. That this behaviour is due to the rapid and quantitative isomerization of the azide to the dibasic nitramine tetrazole, and not to a dibasicity in the azide itself, may be shown by the behaviour of the substance towards silver nitrate solutions after the equivalent of alkali has been added. 5-Nitramine-tetrazole solutions yield with silver nitrate an immediate highly insoluble precipitate of a disilver salt of nitramine tetrazole. On the other hand, nitroguanyl azide solutions on treatment with silver nitrate give a cloudiness. This gradually separates as a crystalline precipitate, but a determination of the excess silver nitrate shows that precipitation is far from complete.

Experimental

The nitroaminoguanidine used in these experiments was prepared by the method of Phillips and Williams[1] and purified by recrystallization from water.

Nitroguanyl azide and nitroguanidine

The source of nitrous acid and the temperature utilized in the preparation of the azide were varied widely. In all cases the same products were obtained in varying relative quantities.

A typical preparation was as follows. 0·05 mole nitroaminoguanidine was suspended in water (25 ml.). The suspension was then heated to 30° with vigorous stirring to effect solution of portion of the substance. 0·05 mole of HCl (*d.*, 1·16) was added and then a solution of sodium nitrite (25 ml., containing 0·05 mole $NaNO_2$) was added dropwise so that the temperature gradually rose to 40°. When the addition of the nitrite solution was complete, the temperature was raised to 60° for five minutes. A fairly vigorous reaction resulted, the nitroaminoguanidine went into solution and the clear solution acquired a yellow colour. The solution was then cooled to room temperature, when a fibrous crystalline mass separated. After allowing this solution to remain at room temperature for 24 hours, it was filtered, the precipitate washed with water and dried in the air. Yield 0·995 g. nitroguanidine.

The filtrate was extracted with 10 ml. portions of ether until the ethereal extracts were colourless. The combined extracts were evaporated at room temperature and the crystalline residue of nitroguanyl azide which resulted dried *in vacuo* over calcium oxide. Yield 1·94 g. It consisted of colourless plates which are readily soluble in ether, fairly soluble in water, alcohol, chloroform and acetone, and insoluble in benzene and carbon disulphide. On heating it melts with slight decomposition at 56° but the decomposition temperature varies somewhat with the rate of heating.

Found: C, 9·3; H, 1·5; N, 64·5, 64·9; Calc: for $CH_0N_2O_2$ C, 9·2, H, 1·5; N, 64·6%.

Nitroguanidine obtained was identified by its characteristic appearance, its decomposition temperature (243°), by a positive reaction to the fuscia colouration, by reduction tests[9] and by a nitrogen estimation. (Found: N = 54·3; Theory, N = 53·8%.)

Disodium, 5-nitramine tetrazole.—Nitroguanyl azide (1·12 g., 0·0086 mole) was added to a solution (10 ml.), containing 1·41 g. sodium acetate (1·41 g., 0·0172 mole). The resulting clear yellow solution was refluxed for one hour.

On cooling, an interlocking mass of needle-shaped crystals separated during three days and a strong odour of acetic acid was detectable. The crystals were separated, washed with alcohol and dried in air. They were highly soluble in water, very slightly soluble in ether, alcohol and benzene and insoluble in acetone, carbon disulphide and chloroform. On heating they exploded with violence and a bright yellow flash at 207°. This agrees with the observation of Benson[10] that tetrazoles, substituted in the 5 position with a nitrogen chain, are explosive. Owing to the explosive nature of the compound, a complete combustion analysis was not made. (Found: N = 47·9. $CN_6O_2Na_2$ requires N, 48·2%.) Yield 1·0 g.

5-Nitramine tetrazole.—0·5 g. Nitroguanyl azide (0·5 g.) was dissolved in water (10 ml.) and 0·5 N. ammonia solution (10 ml.) added. The resulting solution was refluxed until no odour of ammonia could be detected (1½ hours). The solution was then evaporated to half bulk and on its remaining during one day at 0° C., oblong, colourless crystals had separated. These were separated and dried in air. They are fairly soluble in water and insoluble in alcohol, acetone, ether, chloroform and benzene. They melt at 195° and explode at slightly higher temperatures. (Found: N, 64·5, 65·0. $CN_6H_2O_2$ requires N, 64·6%.) Yield 0·42 g.

Reduction of 5-nitramine-tetrazole.—A 25% aqueous solution of 5-nitramine-tetrazole was diluted with its own volume of glacial acetic acid, and excess of zinc dust was added and the temperature maintained at 60° for ten minutes. After decantation from excess zinc, the resultant solution gave, after agitation with benzaldehyde, a colourless precipitate which, after thorough washing in air, gave a positive acridine-hydrochloride spot test for zinc ion. A micro-estimation of zinc was made. (Found: Zn, 26·1, 26·2. $C_8H_6N_6Zn$ requires Zn, 26·0%.) Benzylidene-tetrazolyl hydrazone (m.p., 233°) was obtained on prolonged digestion of the zinc derivative in dilute HCl.

Action of acidified potassium iodide on nitroguanylazide.—Potassium iodide crystals were dissolved in 20 ml. of a standard azide solution containing 0·3084 g. azide per 50 ml. On acidification and boiling, iodine equivalent to 28·7 ml. 1·40 N/20 sodium thiosulphate was liberated. The end-point to the thiosulphate titration was not very sharp.

(Equivalent of azide with respect to iodine liberation, 61·25. Theory for 2 atoms iodine/mol. azide, 65.)

Action of alkali on nitroguanylazide.—Nitroguanylazide solution (5 ml.), containing 0·3084 g. per 50 ml. solution, on titration with 1·14 N/20 carbonate-free alkali, with phenolphthalein as indicator, gave a sharp end-point after the addition of 7·9 ml. alkali. (Equivalent with respect to alkali: 68·5. Repetitions of this experiment gave values for the equivalent which varied between 68 and 69·5.)

Interaction of silver nitrate and disodium nitramine tetrazole.—0·961 N/20 $AgNO_3$ (60 ml.) was added to disodium nitramine tetrazole solution (20 ml.), containing 0·2464 g. per 50 ml. The gelatinous precipitate immediately formed was separated and in a Volhard titration the filtrate gave a sharp end-point after the addition of 36·1 ml. 1·0 N/20 NH_4CNS. (Equivalent with respect to interaction with $AgNO_3$: 91·6. Theory requires M.W. 174.)

Similar experiments with nitroguanyl azide gave much higher values for the equivalent which varied with the relative molar ratios of the $AgNO_3$ and azide employed.

Interaction of nitroguanyl azide and silver nitrate after equivalent of alkali has been added.

Nitroguanyl azide solution (5 ml., containing 0·3084 g. per 50 ml.) was exactly neutralized with 7·9 ml. 1·14 N/20 alkali and 1·0 N/20 $AgNO_3$ (20 ml.) was then added. Immediately a white gelatinous precipitate separated. On filtration the filtrate required 9·3 ml. 1·0 N/20 NH_4CNS. (Equivalent with respect to $AgNO_3$, 57·6).

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THE TRANSFER OF DDT TO FOODSTUFFS FROM IMPREGNATED SACKING

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A method is described for determining the amount of DDT in foodstuffs, using monoethanolamine to dehydrochlorinate the DDT, followed by electrometric titration of the free chloride with silver nitrate; the monoethanolamine does not hydrolyse the fats and oils. The method has been used to determine the quantities of DDT transferred from DDT-impregnated sacking to wheat, wheat flour, soya flour, decorticated groundnuts, and cocoa beans. Relatively large quantities of DDT may be transferred in a few months, particularly to finely divided and fatty foodstuffs, and much caution must be exercised in making recommendations for the use of DDT-impregnated sacks to prevent or control insect infestation in stored foodstuffs. The importance of vapour-phase transfer of DDT is discussed.

It is not surprising that the newer synthetic insecticides have been put to practical use without full knowledge of the toxicological risks, when the urgent need to get the maximum benefit from all possible control measures is borne in mind. The hazards of acute poisoning are usually not difficult to assess, whereas those of chronic poisoning over very long periods of exposure involve research of a most difficult and painstaking kind. Particular care in the use of insecticides must clearly be taken when they are applied to prevent or control infestation in foodstuffs, and the care must be the greater when these materials are used under indoor conditions favourable to their stability and persistence.

Whilst the long-term toxicological work has been in progress, a considerable amount of information has been published upon the value of such insecticides as DDT and benzene hexachloride for the treatment of stored foodstuffs and the premises in which they are kept. No information has yet been published, however, upon the degree of contamination likely to occur when stored products are stowed in contact with surfaces treated with these new synthetic insecticides.

A study has recently been made at the Pest Infestation Laboratory of the value of impregnation of sacking with 1% and 5% by wt. of DDT for protecting the enclosed grain, flour, etc., from insect infestation.[1] Some complementary work has now been completed on the transfer of DDT from such impregnated sacking to foodstuffs stored in contact with it. This paper describes a method for the determination of small quantities of DDT in the presence of the relatively large amounts of fats and oils simultaneously extracted from some foodstuffs and gives the results so far obtained.

Chemical determination of DDT

The method was first worked out for the assay of small quantities of DDT in whole wheat and was later shown to be suitable for the assay of DDT in groundnuts, cocoa beans, and soya flour, foodstuffs of high fat content. The determination was carried out in the following stages—(*a*) removal of DDT from the foodstuff with pure, dry benzene; (*b*) evaporation of the benzene from an aliquot volume of the extract, (*c*) dehydrochlorination of the DDT residue with a solution of monoethanolamine in ethylene glycol monoethyl ether, liberating as Cl^-, one of the five chlorine atoms in the DDT molecule; (*d*) electrometric titration of the liberated chloride with standardized $AgNO_3$ solution.

Reagents

Benzene.—Owing to a temporary shortage of A.R. benzene, the crystallizable grade was used but had to be freed from sulphur compounds, other than thiophene. A satisfactorily pure reagent was prepared by refluxing crystallizable benzene with 1·5% v/v monoethanolamine for 3 hr. During refluxing H_2S was lost through the condenser. The benzene was then