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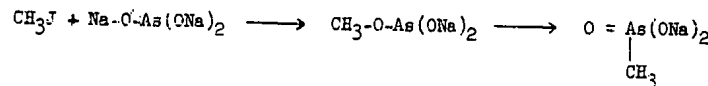
DIADIC TAUTOMERISM /SYNTHESIS OF ORGANIC COMPOUNDS OF PHOSPHORUS AND ARSENIC/

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[This paper deals with the synthesis of substances which may be used as initial materials in the preparation of chemical warfare agents.]

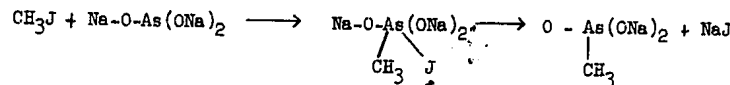
The mechanism of the formation of structurally anomalous alkylation products of salts of hydrocyanic, nitrous, sulfurous, and arsenous acids (Meyer reaction), of the salts of incomplete esters of phosphorous acid (Michaelis - Arbuzov reaction), and of the arylation of salts of arsenous acid (Barth reaction) are explained by different authors in various ways.

The first explanation is based on the assumption of the isomerization of the originally forming normal substitution products, e.g.,



However, the experiments showed that such isomerizations do not take place under the conditions of the alkylation reaction.

The second explanation is considerably more important. It is based on the assumption of the formation of intermediate addition products which are then split up in a different way, e.g.,

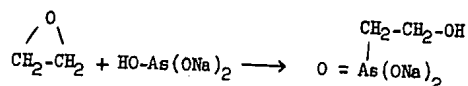


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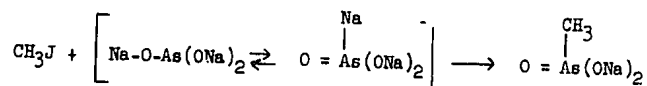
50X1-HUM

However, this method of explanation is inapplicable to the addition reaction of bisulfite to aldehydes, ketones, or ethylene oxide, in which sulfonic acids are formed. To convince ourselves of the fact that such addition is not a characteristic of sulfurous acid only, we performed addition reactions of nitrous, arsenous, and phosphorous acid to ethylene oxide and obtained, respectively, a nitro compound, arsonic acid, and phosphonic acid, e.g.,

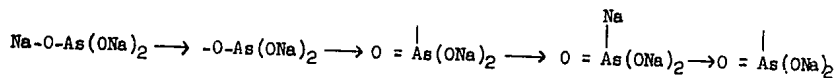


2-nitroethanol was determined in the form of a complex with diazobenzene, hydroxyethyl arsonic acid in the form of β -chloroethyl-dichloroarsine, and diethyl ester of β -hydroxyethyl phosphonic acid by spectral analysis. In the reactions enumerated, there can be no intermediate addition products, and, consequently, drawing on them for an explanation of the substitution reaction is meaningless; in all cases the carbon residue reacts directly with the nitrogen, arsenic, sulfur, or phosphorus, taking the place of hydrogen or metal.

The third method of explanation of the above reactions is based on the assumption of participation in them of salts with pseudomeric structures, e.g.,

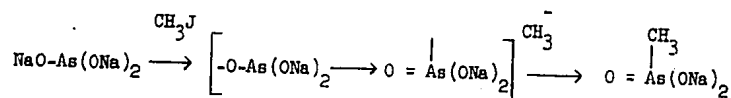


The possibility of the existence of unmeasurably small quantities of pseudomeric structures in equilibrium with the main structures cannot be excluded. However, if it is borne in mind that dissociations of molecules



precede the linking of the residues in new arrangements, then it becomes obvious that due to the equivalence of the third and fifth structures, participation in the transformation of the fourth structure is not essential.

The best explanation of the structurally anomalous substitution and addition reaction is obtained by the concept of ion transformation, e.g.,



In conclusion, it must be pointed out that the concept of a resonance ion does not exclude isomeric ions whose reality is confirmed by their fixation in the original and final molecules.

- 2 -

S-E-C-R-E-T**SECRET**

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50X1-HUM

Experimental Part1. β -Nitroethyl Alcohol

In a flask with an agitator, 23.2 g of magnesium nitrite (0.2 mols) were mixed with 200 ml water; then ethylene oxide was passed in until the weight increased by 10 g (0.23 mols); the reaction mass was cooled in such a manner that the temperature did not exceed 40° C. After standing for 20 hr, the reaction mass was diluted to three times its volume with water and treated at 0° C (cooling by ice) with a 0.1 normal solution of phenyl diazonium in a slightly alkaline medium until the appearance in the solution of an excess of diazonium (test with β -naphthol). The dyestuff was filtered out, washed with water, and dried in the desiccator. The yield was 6 g, i.e., 16% of the theoretical amount calculated on the basis of the nitrite used. After re-crystallization from ligroin (under treatment with carbon), red needle-like crystals were obtained, which were insoluble in water, soluble in alcohol and in ether, and corresponded in their properties to the product obtained by another method by Demuth and Meyer [1].

Analysis:

3.176 mg substance; 0.61 ml N₂ (20°, 736 mm)

Found: 21.62% N

Percentage of N calculated for C₈H₉O₃N₃: 21.54

In the condensation of ethylene oxide with sodium nitrite in a weakly acidic medium, the yield of dyestuff is lower than in the previous case; addition of magnesium sulfate increases the yield of the product.

2. β -Hydroxyethyl Arsonic Acid

Twenty grams of arsenous anhydride (0.1 mols) and 34 g of potassium hydroxide (0.6 g/mol) were stirred in 100 ml water until fully dissolved, and then ethylene oxide was added during a 2-hr period, until the weight had increased by 10 g (0.23 mols). After the reaction mass had been left standing for 20 hr, it was diluted with 200 ml water, acidified with 10% sulfuric acid until the reaction became slightly acidic, and filtered and evaporated in vacuum (not above 50° C) to a viscous liquid (the inorganic salts precipitating during evaporation were filtered out). The viscous liquid was treated with absolute alcohol and the alcohol extract evaporated in vacuum; there was a residue of 16 g of a viscous transparent liquid which formed a precipitate upon heating with magnesia mixture.

For purposes of determination, the product was converted to β -chloroethyl-dichloroarsine. The viscous liquid was diluted with 30 ml water, a small potassium iodide crystal was added, and the solution was saturated with sulfur dioxide at a temperature below 50° C. After the solution had been left standing for 48 hr, a stream of SO₂ was bubbled through it. The light-colored oil which precipitated was separated and mixed with 20 ml carbon tetrachloride. The carbon tetrachloride was driven off in vacuum. The residue (7 g) was treated with 7 g of thionyl chloride (violent reaction) and the product was distilled in vacuum. The boiling point was 79 to 80° C at 12 mm pressure and 93 to 95° C at 32 mm pressure. Six grams of substance were obtained, which had the properties of β -chloroethyl-dichloroarsine [2]. The yield was approximately 30 percent of the theoretical.

During the bubbling of ethylene oxide into a Na₂HAsO₃ solution, very little hydroxyethyl arsonic acid is obtained, and none at all from ethylene oxide and NaH₂AsO₃.

- 3 -

S-E-C-R-E-T

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50X1-HUM

3. *o*-Hydroxyethyl Phosphonic Acid

To 13.9 g (0.1 mol) of diethyl phosphite dissolved in 120 ml absolute alcohol, 2.3 g (0.1 mol) of sodium powder prepared by the Bruell method were added. Ethylene oxide was passed into the mixture under stirring until the weight had increased by 4.5 g (0.1 mol), whereupon the precipitate of sodium diethyl phosphite disappeared. After stirring for one hour, 6.1 g of glacial acetic acid were added, drop by drop, to the mixture, the sodium acetate precipitate was filtered out, and the ester was distilled off (on a water bath, not above 50° C).

The sirupy residue was filtered off under section from a small quantity of acetate and dried in the desiccator over sulfuric acid. A total of 7.6 g of substance were obtained, in which carbon, hydrogen, and pentavalent phosphorus were determined qualitatively. The product was soluble in alcohol and ether. It was distilled in vacuum at 9 mm and 120-130° C and distilled under strong decomposition.

On our request, Gofshteyn and Setkina carried out a spectral analysis. In the infrared spectrum, the following bands were observed: 800 (strong), 880 (medium), 955 (strong), 980 (strong), 1,040 (strong), 1,080 (strong), 1,210 (strong), 1,250 (weak), 1,400 (medium), 140 (weak). The 1,210-1,250 bands must be attributed to the P = O (P→O) bond, since the same frequency is observed in phosphorus oxychloride and other compounds of P...

Summary

1. It is shown that ethylene oxide combines with the nitrogen, arsenic, and phosphorus of nitrous, arsenous, and phosphorous acid, respectively.
2. The question of the mechanism of formation of structurally anomalous alkylation products (by replacement or addition) of salts of hydrocyanic, nitrous, and sulfurous acids, as well as the mechanism of the Meyer-Barth and Michaelis-Arbuzov reactions, are discussed. Unsatisfactory explanations for the mechanism of the above reactions were rejected, and the best explanation was selected.

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2. Gouch and King: *Journ. Chem. Soc.*, 1928, p 2432; Scherlin and Epstein, *Berichte*, Vol 61, p 1921, (1928)

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- 4 -

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