Synthesizing phosphorus hydrazones as a method to dispose unsymmetrical dimethylhydrazine

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Abstract. This paper deals with studying the possibility of obtaining a phosphorus-containing derivative of acetone N,N-dimethylhydrazine. It is shown that the phosphorylated derivative is not obtained by directly phosphorylating the acetone dimethylhydrazine, but via Abramov reaction from aminoacetone that is afforded in the interaction of diphenylphosphorous acid with the acetone N,N-dimethylhydrazine.

In modern times, rocket and space equipment takes a heavy toll on the environment. Soil is primarily affected by it due to the large amounts of unburnt propellants that penetrate it when the expended rocket stages fall. Such territories turn out to be burnt out and unsuitable for the existence of living organisms. Moreover, various failures or computational errors cause accidents at rocket launches, which also contributes to environmental contamination. Therefore, developing environmentally sound fuels, as well as improving flight-vehicle designs, can considerably reduce the biosphere load [1-3].

Unsymmetrical dimethylhydrazine (UDMH, 1,1-dimethylhydrazine, N,N-dimethylhydrazine, heptyl) is a liquid propellant component that is highly toxic for the entire biological envelope. It is well known that the military ground stocks of this component worldwide amount to the hundreds of thousands of tons, which is a dire threat to all mankind. As of today, the issue of disposing this compound is really acute. Studies continue regarding the possibility of using UDMH in various sectors of national economy. However, the attempts to use 1,1-dimethylhydrazine have not moved beyond research activities or implemented in industry.

Works are known regarding the use of UDMH in producing thermoset polymers used as glues or sealants in manufacturing emulsion paints and colors with increased corrosive and chemical resistance. Based on UDMH and crosslinked chloromethylated polystyrene, new types of anionites were obtained, which 4-5 times exceed the known anion-exchange resins in their volume capacity. Based on heptyl, an efficient cardioprotective and immunomodulatory pharmaceutical, Mildronate, was developed [4].

Studies previously performed at the Department of Engineering Ecology allowed us to extend our knowledge in the chemistry of unsymmetrical dimethylhydrazine and its organophosphorus derivatives.
This paper is aimed at studying the possibility of obtaining the phosphorylated derivative of acetone N,N-dimethylhydrazine in interacting with diphenylphosphorous acid (DPPA). These objects are selected based on the results of our previous studies [5-7].

To avoid forming saltlike-structure compounds in the Pudovik reaction, which were registered in the interaction of the N,N-dimethylhydrazones of various aldehydes with dialkylphosphorous acids, we decided to investigate diphenylphosphorous acid (DPPA) that does not usually get dealkylated by highly basic compounds. To avoid forming nitrils resulting from breaking the N-N bond of the dimethylhydrazones of arylaldehydes, acetone dimethylhydrazine was studied in the Pudovkin reactions.

Acetone does not react with UDMH without a catalyst. The process was conducted at T=54-60°C within 22 hours; acetone : UDMH = 1:3; catalyst: Sulfuric acid (1 ml). Upon curing, the reaction mass was fractionated. This resulted in separating a product with T<br>97-98°C, nD<br>1.3870, d4<br>0.776, and yield of 23%.

Structure of the compound obtained was proven by elemental analysis and IR spectroscopy techniques, while its purity by the TLC method. In the IR spectrum of the product obtained from acetone reacting with UDMH, there is no absorption band in the area of 1,690 cm<sup>-1</sup>, typical of carbonyl group oscillations, and there is an absorption band in the area of 1,650 cm<sup>-1</sup>, which belongs to the oscillations of the C=N- group. Elemental analysis data correlate well with the computed values of C, H, and N, based on formula C<sub>6</sub>H<sub>10</sub>N.<sup>2</sup>

In view of the above, we can conclude that acetone reacting with UDMH resulted in obtaining acetone N,N-dimethylhydrazine (ADMH). Interaction runs according to the following scheme:

\[
\begin{align*}
\text{CH}_3 & \quad \text{C} \quad \text{CH} + \text{H} \quad \text{N} \quad (\text{CH})_2 \quad \text{N(CH)}_2 \\
\text{O} & \quad \text{H} \quad \text{O} \quad \text{C} \quad \text{CH} \quad \text{C} \quad \text{N(\text{CH})}_2
\end{align*}
\]

The ADMH obtained was studied in the reaction with DPPA. Interaction was conducted in presence of sulfuric acid at the temperature of 98-100°C within 10 hours. Upon curing, the reaction mass was fractionated. This resulted in obtaining a product with T<br>71-72°C / 16 mm. Composition and structure of the compound obtained were proven using elemental analyses and <sup>31</sup>P NMR and IR spectroscopy.

In the <sup>31</sup>P NMR spectrum of the product obtained, there are no signals typical of phosphonate-structure compounds.

In the IR spectrum, intensive signals are observed in the area of 1,700 cm<sup>-1</sup> (C=O) and 3,200-3,400 cm<sup>-1</sup> (NH<sub>2</sub>). Elemental analysis data prove the structure of compound (II) and correlate well with the computed values based on formula C<sub>6</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub>. Thus, the direction of adding the phosphorus component on multiple bond of acetone dimethylhydrazine is not implemented.

Reaction scheme assumed:

\[
\begin{align*}
\text{CH}_3 & \quad \text{C} \quad \text{C} + (\text{C}_6\text{H}_5\text{O})_2\text{P} \\
\text{N} & \quad \text{N(\text{CH})}_2
\end{align*}
\]

Aminoacetone (II) obtained in this manner is of interest as a synthon for obtaining oxyprophonates by the Abramov reaction.

For this purpose, aminoketone was introduced into the reaction with DPPA. The process was conducted at the temperature of 120-130°C within 6 hours. By fractionating the reaction mass, we separated a fraction with the boiling point of 53-54°C / 20 mm. Composition and structure of the compound obtained were proven using elemental analyses and <sup>31</sup>P NMR and IR spectroscopy. Chemical shift of the phosphorus nucleus in compound (III) lies within δ<sub>P</sub>=14 ppm, which corresponds with phosphonate.
IR spectrum, there is not absorption band in the area of 1,700 cm\(^{-1}\), typical of carbonyl group oscillations, and there are intensive absorption bands (\(\nu\), cm\(^{-1}\)): 3,200-3,400 (NH\(_2\)), 1,280 (P=O), 1,580, 1,500, and 750 (benzene ring), and 3,400-3,600 (OH). Elemental analysis data prove the structure of the compound and correlate well with the computed values, based on formula \(\text{C}_{15}\text{H}_{18}\text{NO}_3\text{P}\). Thus, compound (III) is the diphenyl ether of 1-methyl-1-aminomethyl-1-hydroxymethyl phosphonic acid.

Reaction scheme assumed:

\[
\text{CH}_3 \equiv \text{C} \equiv \text{CH}_2\text{NH}_2 + (\text{C}_6\text{H}_5\text{O})_2\text{P} \xrightarrow[\equiv \text{O}]{} \text{CH}_3 \equiv \text{C} \equiv \text{CH}_2\text{NH}_2
\]

III

Physical and chemical constants of compounds I - III are shown in Table 1.

| Compound | Found, in % | Formula | Computed, in % |
|----------|-------------|---------|----------------|
|          | C   | H   | N   | P   | C   | H | N | P |
| I        | 60.1 | 12.2 | 27.2 | -   | 60.0 | 12.0 | 28.0 | -  |
| II       | 51.3 | 10.6 | 19.3 | -   | 49.3 | 9.6 | 9.2 | - |
| III      | 57.6 | 5.9  | 4.3  | 9.5 | 58.6 | 5.8 | 4.5 | 10.0 |

Thus,
1. In the interaction of acetone with unsymmetrical dimethylhydrazine, acetone (I) N,N-dimethyl-hydrazine was obtained.
2. Reaction of acetone dimethylhydrazine with diphenylphosphorous acid was conducted in presence of sulfuric acid. It is shown that the direction of adding DPPA by the C=N bond of dimethylhydrazine is not implemented. The reaction runs with building up aminoacetone (II).
3. As a result of interaction between aminoacetone and DPPA, we obtained the diphenyl ether of 1-methyl-1-aminomethyl-1-hydroxymethylphosphate acid (III).

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