EFFECT OF PRESSURE ON THE THERMAL DECOMPOSITION OF METHYLTRIPHENOXYPHOSPHONIUM IODIDE

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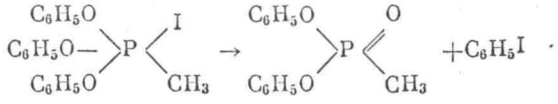
In our studies [1, 2], it was demonstrated that pressure extremely substantially accelerates the Arbuzov reaction; moreover, it was hypothesized that the observed effect is due to the influence of pressure on the first step of the reaction. An unambiguous answer to this question would necessitate at least a qualitative determination of the influence of pressure on the second step of the reaction; this was the purpose of this work. In it we studied the thermal decomposition of methyltriphenoxyphosphonium iodide—the stable intermediate addition product in the reaction of rearrangement of the phenyl ester of phosphorous acid in the presence of methyl iodide [3]



EXPERIMENTAL SECTION

Methyltriphenoxyphosphonium iodide was produced by heating a mixture of triphenyl phosphite and methyl iodide in a sealed glass ampoule at 130° for 2.5 h [4, 5]. After two recrystallizations from a mixture of throughly dried dichloroethane and ether, we obtained white crystals with m. p. 140°. Literature data [4]: m.p. 130°; [6]; m. p. 146°. Found: I 28.45; 28.30; 28.17%. $C_{19}H_{18}O_3PI$. Calculated: I 28.10%.

Experiments on thermal decomposition were conducted at 200 ± 0.2° at the saturated vapor pressure of the initial compound, as well as at a hydrostatic pressure of 2000 kg/cm^2. In the first case, the substance was placed in a glass ampoule, which was then sealed. Experiments at high pressure were conducted in a steel vessel specially designed for this purpose, into which a Teflon ampoule with the starting material was placed (the construction of the ampoule is described in [7]). An initial oil pressure of 820 kg/cm^2 was created in the vessel with a NZhR pump, after which the vessel was placed in a thermostat heated to the temperature of the experiment; then the oil pressure was raised to 2000 kg/cm^2 in a period of several minutes, and remained constant during the entire experiment (19 h). Then the thermostat was cooled by passing cold water through a coil placed in it. All the operations with the starting material, as well as opening of the glass and Teflon ampoules, were performed in a stream of dry nitrogen. In the experiments in a glass ampoule, the amount of substance loaded was ~ 11 g, and in the Teflon ampoule ~ 8 g. The reaction products were also distilled in a stream of dry nitrogen; the fraction with b. p. 71-72° (14 mm), containing iodobenzene with a small admixture of phenol (~ 1% by weight of the starting material) was distilled off. The iodobenzene and phenol contents in this fraction were determined according to the coefficient of refraction from a calibration curve "n_D^{20} versus percent by weight phenol." After distillation of the indicated fraction, the residue was treated with absolute ethanol; under these conditions all the unreacted methyltriphenoxyphosphonium iodide is converted to an ester of methylphosphinic acid, with the simultaneous formation of ethyl iodide and phenol [3]. Then the mixture of ethyl iodide and unreacted ethanol was distilled off, after which the phenol was distilled off under vacuum; the fraction of unreacted initial compound was judged according to the amount of phenol. In the thermal decomposition of methyltriphenoxyphosphonium iodide, certain side reactions also take place—resinification, isolation of iodine, and formation of small amounts (1-2% by weight) of benzene. The experimental results are summarized in the Table.