The ability of a number of compounds (acetyl perchlorate, iodine, phosphorus oxychloride, and phosphorus pentachloride) to detach a hydride ion from the meso carbon atom of 1,5-diketones that are formed in the condensation of acetals with ketones and are cyclized to symmetrical pyrylium salts was studied.

As was recently demonstrated, the reaction of the acetals of aldehydes and methyl ketones in the presence of triphenylmethyl perchlorate (I) gives 1,5-diketones, which subsequently lose a hydride ion under the influence of I and are cyclized to symmetrical pyrylium salts [1].

The next step in the study of this reaction was an investigation of the ability of a number of substances (acetyl perchlorate, iodine, POC13, PC15, etc.) to catalyze the formation of saturated 1,5-diketones with subsequent detachment of a hydride ion and cyclization to pyrylium salts. Instead of using I as the hydride-ion acceptor, we used acetyl perchlorate (II), which, as is well-known, converts 1,5-diketones to pyrylium salts in good yields [2,3]. We were able to show that II completely successfully catalyzes the crotonic condensation of aldehyde acetals with methyl ketones and the subsequent Michael condensation to give saturated 1,5-diketones. In the next step of the process, II acts like I, stripping a hydride ion from the 1,5-diketones, which are thus converted to pyrylium salts:

\[ \text{CH}_3\text{CO} \text{R'} \rightarrow \text{II} \rightarrow \text{II} \rightarrow \text{HC/CHR} \rightarrow \text{II} \rightarrow [\text{CH}_2\text{C}0\text{H}] \]

The use of II instead of the more difficult-to-obtain triphenylmethyl perchlorate in this reaction seems to us completely justified, since in this case the triaryl-substituted pyrylium salts are obtained in higher yields. Also demonstrated was the possibility of using this method to obtain 2,6-diphenyl-4-methylpyrylium perchlorate (condensation of acetaldehyde acetal with acetophenone) and a γ-unsubstituted pyrylium salt (in the reaction of methylal or ethyl orthoformate with acetophenone). The condensation of cyclo-hexanone with benzaldehyde acetal in the presence of trityl perchlorate and acetyl perchlorate gave 4-phenyl-2,3;5,6-bis(tetramethylene)pyrylium perchlorate in yields of 36.3 and 22.7%, respectively. The data on the yields of the pyrylium salts are presented in Table 1.

It also seemed of interest to attempt to use elemental iodine in this reaction as a condensing agent and hydride-ion acceptor. It was shown that pyrylium periodides are formed as a result of condensation of acetals with acetophenone in the presence of iodine.
The condensation of aldehyde acetals with acetophenone in the presence of iodine (molar ratio 1 : 2 : 1) was carried out by prolonged (3-5 h) refluxing of the components in glacial acetic acid. In the case of the condensation of aromatic aldehyde acetals, the pyrylium salts were obtained in rather high yields (24-48%), while the use of aliphatic acetals led to a considerable reduction in the yields of final products. On the basis of the data on the yields of 2,4,6-triaryl-substituted pyrylium salts, it can be assumed that there is considerable polarization of the bond in the iodine molecule under the experimental conditions, and this polarization makes it possible to effectively bring about detachment of a hydride ion from the 1,5-diketones formed in the process. Unfortunately, many of the periodides obtained are often impure and decompose during purification to liberate iodine. Satisfactory results of elementary analysis could be obtained only for 2,4,6-triphenyl- and 2,6-diphenyl-4-(p-nitrophenyl)pyrylium periodides. The remaining samples were identified as the perchlorates.

The use of iodine enabled us to repudiate the suspicion that the acetals are initially hydrolyzed to aldehydes, and the latter then give pyrylium salts via the usual scheme [1]. Thus exclusion of an acidic medium by using butanol as the solvent gave 39.2% 2,4,6-triphenylpyrylium periodide, which was identical to the product synthesized in acetic acid. Data on the yields of pyrylium salts obtained in the condensation of acetals with methyl ketones in the presence of iodine are presented in Table 1.

An attempt to condense acetals with acetophenone in the presence of phosphorus oxychloride and phosphorus pentachloride gave very low yields of the pyrylium salts (3-5%), which were isolated as the perchlorates [4]. The use of bromine, N-bromosuccinimide, and benzoyl chloride as hydride-ion acceptors did not give positive results at all.

**EXPERIMENTAL**

Application of Acetyl Perchlorate (II). The reagent was prepared immediately prior to the reaction by the dropwise addition of 1 ml of 70% perchloric acid to 3.7 ml of acetic acid with ice cooling. The resulting solution was rapidly added dropwise in 3-ml quantities to a refluxing mixture of acetal, ketone, and glacial acetic acid (in a molar ratio of 2:4:3). After 5-10 min, the mixture was cooled, and the pyrylium salt was precipitated by the addition of ether, removed by filtration, washed with ether, and recrystallized from acetic acid, nitromethane, or acetic acid-nitromethane mixtures.

Pyrylium Periodides. The reaction was carried out by prolonged refluxing (3-5 h, until the evolution of iodine vapors ceased) of a mixture of the acetal, ketone, and iodine (in a molar ratio of 1:2:1) in glacial acetic acid. The mixture was cooled, and the salt was precipitated by the addition of ether. The pyrylium