PHENOLIC DERIVATIVES OF 2-PYRONE. I.

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The condensation of hydroxy- and methoxyacetophenones with 2,1,1,3-tetraehloro-3-ethoxypropane or β,β-dichloroacrolein in an acid medium has yielded a number of dichlorodienyl hydroxyphenyl ketones which are converted into the corresponding 2-pyrone in acetic or propionic acids in the presence of phosphoric acid.

The α-pyrene nucleus is a component of a number of natural and synthetic compounds possessing various physiological effects [1, 2, 3]. It appeared of interest to obtain phenolic derivatives of 2-pyrene and to study the influence of the position of the hydroxy group in the phenolic radical on their physicochemical properties and biological activities.

We synthesized 6-(hydroxyphenyl)-2-pyrone by cyclizing the dichlorodienyl ketones (I-VI) which were obtained, in their turn, by condensing hydroxy- and methoxyacetophenones with 1,1,3-tetrachloro-3-ethoxypropene (TCEP) or with β,β-dichloroacrolein (DCA) by the following scheme:

\[
\begin{align*}
R &\rightarrow R \quad \text{CH}_3 \quad \text{CCI}_3 \quad \text{CHClCH}_2 \quad \text{Cl} \quad \text{H}_2 \quad \text{O} \\
\text{or} &
\end{align*}
\]

I-VI VII-XIII

We found that the synthesis can be carried out in a single stage without the isolation of the dichlorodienyl ketone not only when DCA and 1,1,3-trichloro-3-ethoxypropene are used [4] but also in the case of TCEP; under these conditions the yield of pyrone amounts to 80-90% (Table 2). The hydroxy- and methoxyacetophenones react with TCEP readily even in the cold (Table 1). o-Hydroxyacetophenone is an exception, undergoing only 5-10% reaction under these conditions.

The condensation of this compound with DCA at 40-50 °C increases the yield of 1,1-dichloro-5-(o-hydroxyphenyl)-1,3-pentadien-5-one to 70-80%.

Increasing the temperature and time of the reaction raised the yield of VII and lowered the yield of XIV. Substance XIV was colorless (no conjugated system of bonds), did not dissolve in alkalis, and did not give a reaction with ferric chloride solution. A comparison of the IR spectra of I, VII, and XIV confirmed the structure of the latter (see the figure). The IR spectrum of XIV exhibited an absorption band in the 1688 cm⁻¹ region due to the stretching vibrations of a C=O group and a characteristic band in the 1643 cm⁻¹ region due to the stretching vibrations of an isolated C=O bond of a vinyl group. Moreover, there were strong bands in the 1222 and 1070 cm⁻¹ regions corresponding to the stretching vibrations of the --O=C--O= grouping. There were no characteristic bands for the absorption of a hydroxy group whatever. The absence of bands corresponding to the vibrations of an OH group and the displacement of the band of the carbonyl absorption in the direction of shorter wavelengths in the IR spectrum of I is explained by the existence of a hydrogen bond between the carbonyl group and the phenolic hydroxyl. The IR spectrum of VII clearly shows a broad band of associated hydroxy groups with maxima in the 3070 and 3150 cm⁻¹ region and a strong absorption band (1712, 1690 cm⁻¹) characteristic for an α-pyrene ring [5, 6].

Compounds I, III, VII, and IX smoothly gave acetyl derivatives with acetic anhydride in the presence of pyridine or sodium acetate. Compounds VIII, X, and XII readily underwent demethylation without the cleavage of the pyrone ring to give VII, IX, and XII, respectively, under the action of aluminum chloride in benzene solution. The o- and p-isomers demethylated more easily than the m-isomer. All the dichlorodienyl ketones (apart from II) and α-pyrone obtained consisted of faintly colored crystalline substances difficult to purify. Compounds II and IV were unstable and decomposed on storage with the evolution of hydrogen chloride.

EXPERIMENTAL

1, 1-Dichloro-5-(o-hydroxyphenyl)-1,3-pentadien-5-one (I). Dry hydrogen chloride was passed for 30 min into a mixture of 13.8 g
IR spectra: 1) 1,1-dichloro-5-(o-hydroxyphenyl)-1,3-penta-dien-5-one; 2) 2-(β,β-dichlorovinyl)-4-chromanone; 3) 6-(o-hydroxyphenyl)-2-pyrone.