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THE APPLICATION OF POLYPHOSPHORIC ACID (PPA) IN SYNTHESIS OF 2,6-DIARYLSUBSTITUTED SALTS OF PYRYLIUM AND 3-ARYLSUBSTITUTED ISOCOUMARINS.

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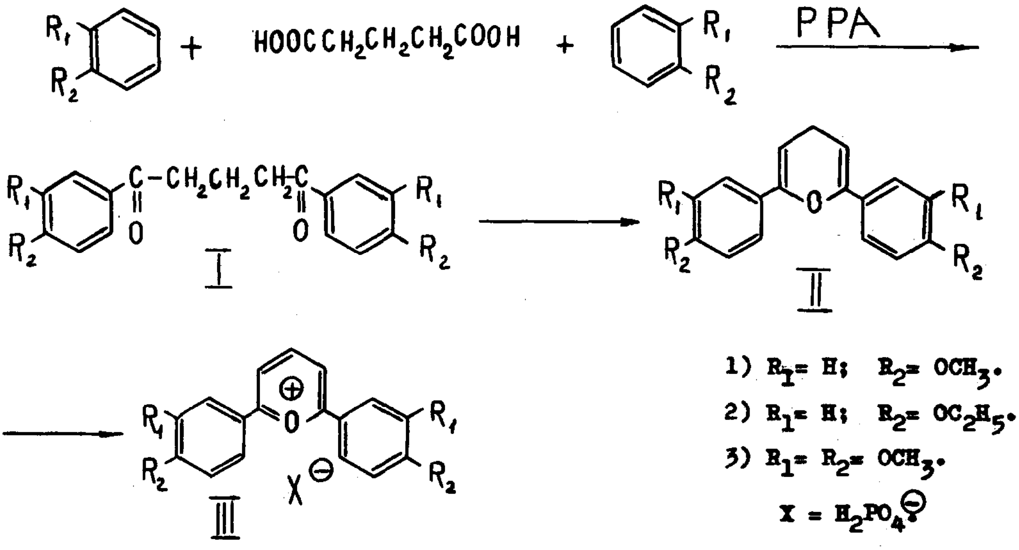
In recent years polyphosphoric acid (PPA) has found ever-increasing use in synthetic organic chemistry. The acylation of phenols and its ethers with PPA has been studied by several investigators.[1-4]

We have studied the reaction of the acylation of phenolic ethers by dicarboxylic acids (glutaric and homophtalic) in the presence of PPA.

2,6-Diarylsubstituted pyrylium salts resulted from the reaction of the acylation of phenolic ethers by glutaric acid in the presence of PPA.



1) R_1= H; R_2= OCH_3.
2) R_1= H; R_2= OC_2H_5.
3) R_1= R_2= OCH_3.
X = $H_2PO_4^{\ominus}$

It is possible that the reaction proceeds by the following mechanism: the enol form of 1,5-diketone (I) cyclizes into 2,6-diarylsubstituted pyran (II) which is converted into 2,6-diarylsubstituted salt of pyrylium (III) with the cleavage of hydride-ion.

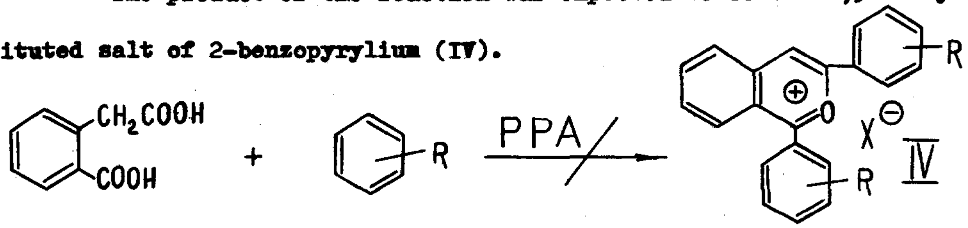
The reaction was carried out by heating the mixture of ether of phenol and glutaric acid at 100°C with 6-10-fold amount of PPA (by weight) for 80 min. with stirring.*

The products of the reaction were isolated in the form of phosphates of pyrylium insoluble in water; they were converted into perchlorates of pyrylium by the action of aqueous perchloric acid.

The obtained salts were identical in infrared spectra, melting points and mixed melting points to the 2,6-diarylsubstituted salts of pyrylium obtained previously[5].

By analogy with the reaction of the acylation by glutaric acid we carried out the acylation of phenolic ethers by homophthalic acid in the presence of PPA.

The product of the reaction was expected to be the 1,3-diarylsubstituted salt of 2-benzopyrylium (IV).



However, only monoacylation proved to be occured with the following cyclizing of the formed o-carboxybenzyl phenyl ketones (V) into 3-arylsubstituted isocoumarins (VI).

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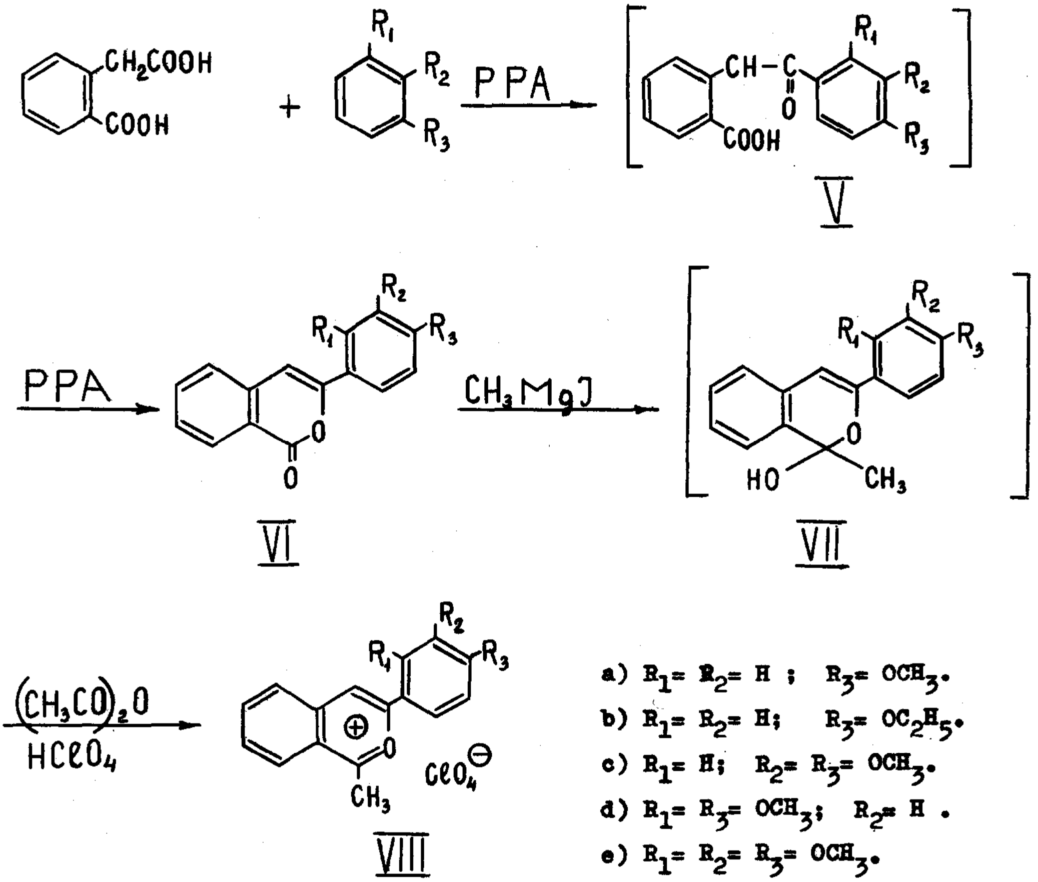
* The application of 70% $HClO_4$ as co- catalyst accelerates the reaction but results in strongly contaminated products.



a) $R_1 = R_2 = H$; $R_3 = OCH_3$.
b) $R_1 = R_2 = H$; $R_3 = OC_2H_5$.
c) $R_1 = H$; $R_2 = R_3 = OCH_3$.
d) $R_1 = R_3 = OCH_3$; $R_2 = H$.
e) $R_1 = R_2 = R_3 = OCH_3$.

The reaction was carried out while heating of the mixture of the ether of phenol and homophtalic acid with 6-8-fold amount of PPA (by weight) at 100°C for 10-60 min. with stirring.

This method has some advantage over previously known methods[6,7] in that 3-arylisocoumarins can be prepared in one stage in a pure state with good yield (60-90%).

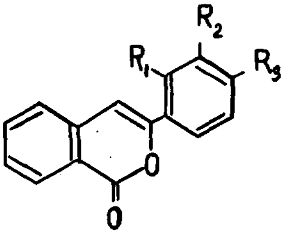


TABLE I

R_1	R_2	R_3	Time of reaction (min.)	Melting points (°C)	Yield (%)	IR-spectra (cm^{-1})
H	H	OCH_3	60	116, 122*	65	1742, 1620, 1275
H	H	OC_2H_5	60	122	60	1734, 1606, 1264
H	OCH_3	OCH_3	60	115	60	1704, 1602, 1275
OCH_3	H	OCH_3	10	171**	93	1708, 1608, 1280
OCH_3	OCH_3	OCH_3	40	108	85	1714, 1604, 1286

*Lit.[7] m.p. 116° then 126°.

**The product was purified by crystallisation from acetic acid. All the rest of isocoumarins were crystallized from ethanol.

The composition of the obtained compounds was confirmed by elementary analysis.

The addition of methylmagnesium iodide to 3-(4′-methoxyphenyl)-isocoumarin (VIa), followed by perchloric acid and acetic anhydride, yields the perchlorate of 1-methyl-3-(4′-methoxyphenyl)-2-benzopyrylium (VIIIa), yellow needles, m.p. 192° from acetic acid, 50% yield. Calcd.: C 58,31; H 4,15; CI 10,42; $C_{17}H_{15}CI\ O_6$ Found: C 58,23; H 4,28; CI 10,13. IR-spectra: 1622, 1606, 1275, 1242 cm^{-1}.

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