HETEROCYCLES, Vol. 20, No 12, 1983

# REACTIVITY OF ARYLCINNAMATES IN POLYPHOSPHORIC ACID (PPA) : CYCLISATION AND REARRANGEMENT REACTIONS

Jean-François E. Dupin and Jacques Chenault*
Laboratoire d'Etude des Composés Phénoliques - U.E.R. de Sciences Fondamentales et Appliquées - Université d'Orléans - 45046 Orléans Cédex - France

Abstract - In polyphosphoric acid (PPA), various phenyl-substituted cinnamates react to give 4-phenyl-3,4-dihydrocoumarins, flavanones or 3-phenylindanone owing to the nature of the substituents on the phenyl moiety.

In a previous paper[1], we have synthesized numerous substituted 4-(methoxyphenyl)-3,4-dihydrocoumarins by reaction of methoxycinnamic acid with various dimethylphenols. The course of the reaction was mainly affected by the methoxy substituent of the phenol moiety of cinnamic acids. Continuing our interest in the synthesis of phenyldihydrocoumarins, these results led us to study the reactivity of aryl-substituted cinnamates (in PPA) obtained from cinnamoyl chloride with substituted phenols.

The esters have been synthesized by the following procedure. In a solution of 0.12 mole of the phenol and 0.12 mole of pyridine in 100 ml of anhydrous benzene is added, under stirring, 0.12 mole of cinnamoyl chloride in 30 ml of anhydrous benzene. The mixture is heated during one hour on a water bath. After filtration and evaporation of the solvant, we obtained the cinnamates in solid state with about 99 % yield. With this procedure we have prepared : 4-nitrophenyl-, phenyl-,4-chloro-3,5-dimethylphenyl-,3,5-dimethylphenyl-,3,5-dimethoxyphenyl-,2-methoxyphenyl-, 3,4,5-trimethoxyphenyl-,4-acetylphenyl-,3,5-dichlorophenyl- and 2,4-dimethylphenyl cinnamates. To a mixture of 80 g of $P_2O_5$ and 96 ml of concentrated $H_3PO_4$ (85 %, d = 1.695) stirred at 80°C were added 0.033 mole of the ester. After one hour and a half, the mixture was pourred on 500 g of crushed ice. The aqueous phase was extracted several times with chloroform. The continuation of the treatment has been done like those described in reference 1. We obtained products whose structure has been confirmed by spectroscopic data (IR, NMR). Our results are summarized in table I.

Table I

Reactivity of phenyl-substituted cinnamates

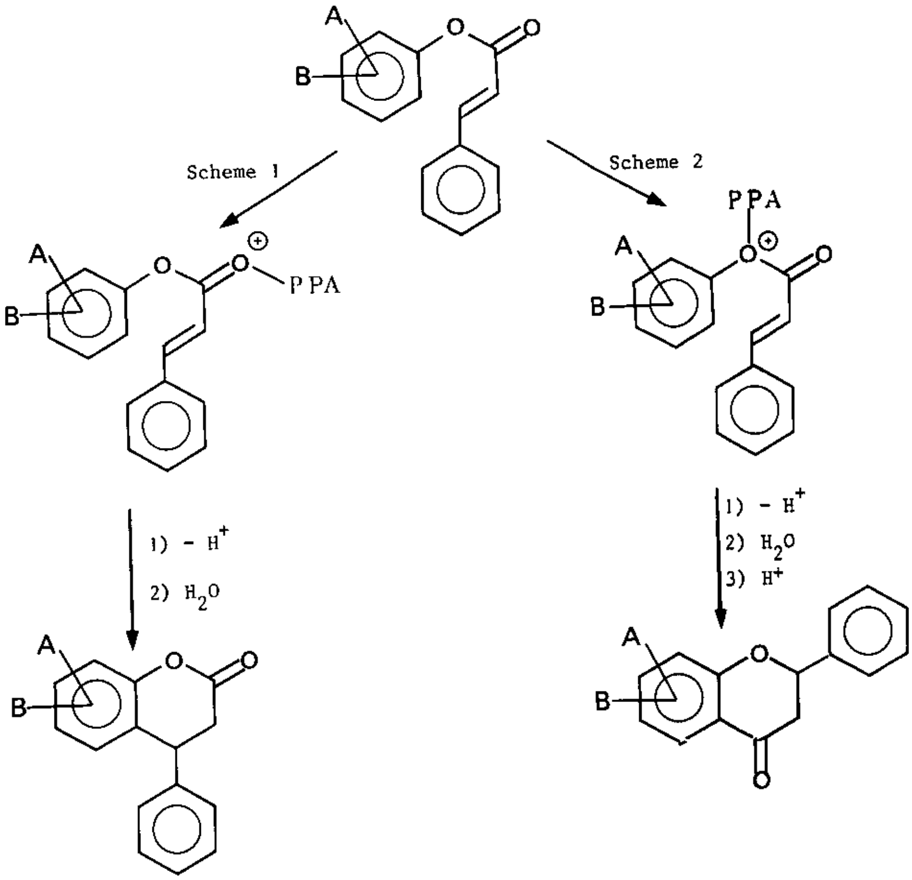
in PPA during 1.5 h at 80°C

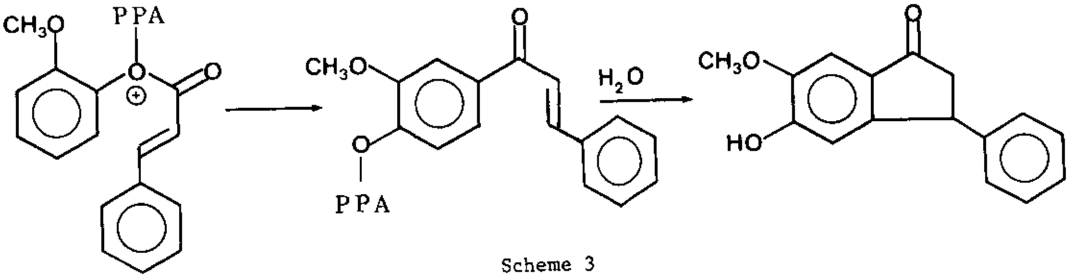
| Cinnamates | Products | mp °C | Yield (%) |
|---|---|---|---|
| phényl | none | - | - |
| 4-nitrophenyl | none | - | - |
| 4-acetylphenyl | tars | - | - |
| 4-chloro-3,5-dimethylphenyl | 6-chloro-5,7-dimethyl-4-phenyl-3,4-dihydrocoumarin | 137 | 60 |
| 3,5-dimethylphenyl | 5,7-dimethyl-4-phenyl-3,4-dihydrocoumarin | 134 | 90 |
| 3,5-dichlorophenyl | 5,7-dichloro-4-phenyl-3,4-dihydrocoumarin | 128 | 40 |
| 2,4-dimethylphenyl | 6,8-dimethyl-4-phenyl-3,4-dihydrocoumarin | 106 | 66 |
| 2-methoxyphenyl | 5-hydroxy-6-methoxy-3-phenylindanone | 148 | 22 |
| 3,5-dimethoxyphenyl | 5,7-dimethoxyflavanone | 138 | 24 |
| 3,4,5-trimethoxyphenyl | 5,6,7-trimethoxy-4-phenyl-3,4-dihydrocoumarin | 152 | 54 mixture |
|  | 5,6,7-trimethoxyflavanone | 160 |  |

We can explain these results as follow.

The phenyl cinnamate forms a coordination complex with PPA with the more nucleophilic oxygen atom of the ester group. Three cases are possible.

When electron withdrawing substituents ($-NO_2$, $-COCH_3$) are present on the phenoxy part of the ester, the coordination complex is formed with the carbonyl oxygen atom of the ester group but, by deactivation of the benzene ring no reaction occurs. It is the same when the ring is unsubstituted.





Scheme 3

When weakly donating substituents (-$CH_3$) or electron donating or withdrawing substituents (-Cl) are present, the carbonyl oxygen atom of the ester group is yet complexed with PPA, the benzene ring is weakly activated in ortho position : we obtain a phenyldihydrocoumarin by Friedel-Crafts cyclisation (scheme 1).

When good electron donating substituents are present ($CH_3O$-) then appears a nucleophilic center on the benzene ring in ortho position with regard to the ester group. This negative charge increases the nucleophicity of the phenoxy oxygen atom by field effect. Fries transposition is possible and we obtain a flavanone (scheme 2).

In the special case of methoxy-2-phenyl cinnamate,after complexation of the phenoxy oxygen atom, acylium ion formed during Fries rearrangement can react in para position with regard to the hydroxyl group, in the absence of steric hindrance (the same phenomenon was observed by Grant[2] when he studies reaction of o-cresol and guaïacol with crotonic acid in PPA). A phenyl-3-indanone is then formed (scheme 3).

REFERENCES AND NOTES

1. J. Chenault and J.F.E. Dupin, Heterocycles, 1983, **20**, 437.
2. H.G. Grant, Z. Naturforsch., 1979, **34b**, 728.

Received, 18th July, 1983