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Synthesis and investigation of 2- hydroxyaryl(5-methylfur-2-yl) alkanes.

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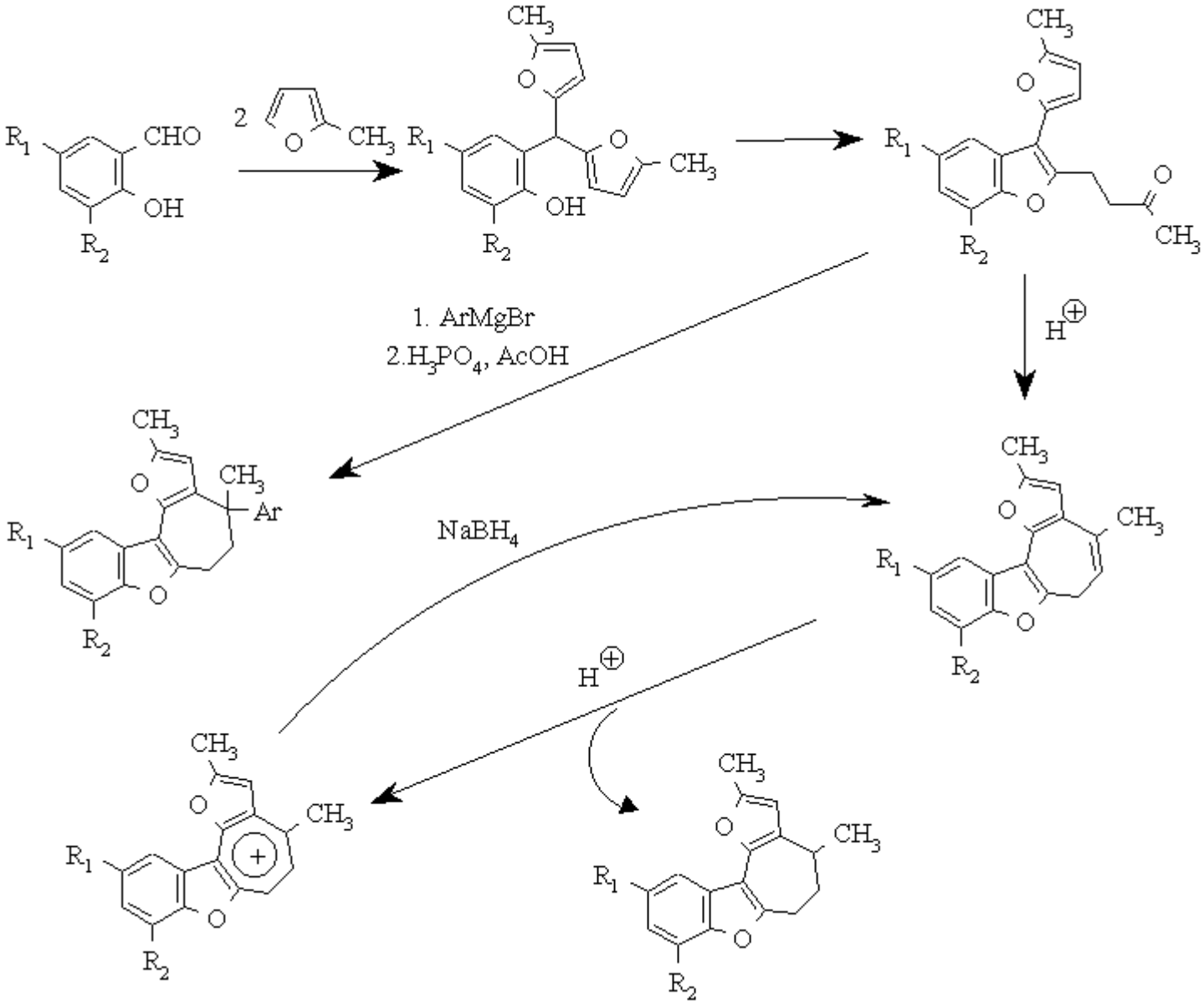
With biographical summary

Abstract: The title compounds were synthesised by furan alkylation with various 2- hydroxybenzyl alkohols. Route to various derivatives of 3-R-2-(3-oxobutyl)benzo[b]furan was shown. The synthesis of dibenzoxazulenium derivatives was attempted.

Keywords: 2-methylfuran, 2-hydroxyarylfurylmethanes, benzofuran, oxazulene derivatives.

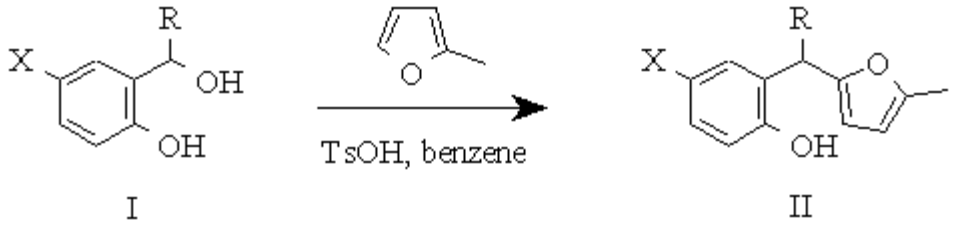
Introduction

It was shown by the authors in previous studies that 2- hydroxyarylbis(5-methylfur-2-yl)methanes, readily obtainable by sylvane and salicilaldehydes condensation catalysed by trimethylchlorosilane or boric acid [1], can undergo rearrangement into 3-(5-methylfur-2-yl)-2-(3-oxobutyl)benzo[b]furan derivatives under the treatment of ethanolic hydrogen chloride solution [2]. The latter compounds can serve as a precursors of benzo[b]furo[2,3-h]-1-oxazulenium salts both by trityl perchlorate oxidation and disproportion in the presence of perchloric acid [3,4].



Results and Discussion

In the present paper we try to extend the scope of such reaction. Starting from various 2- hydroxybenzyl alkohols and 2-hydroxybenzhydrols I corresponding 2-hydroxyaryl(5-methylfur-2-yl)alkanes II were obtained:

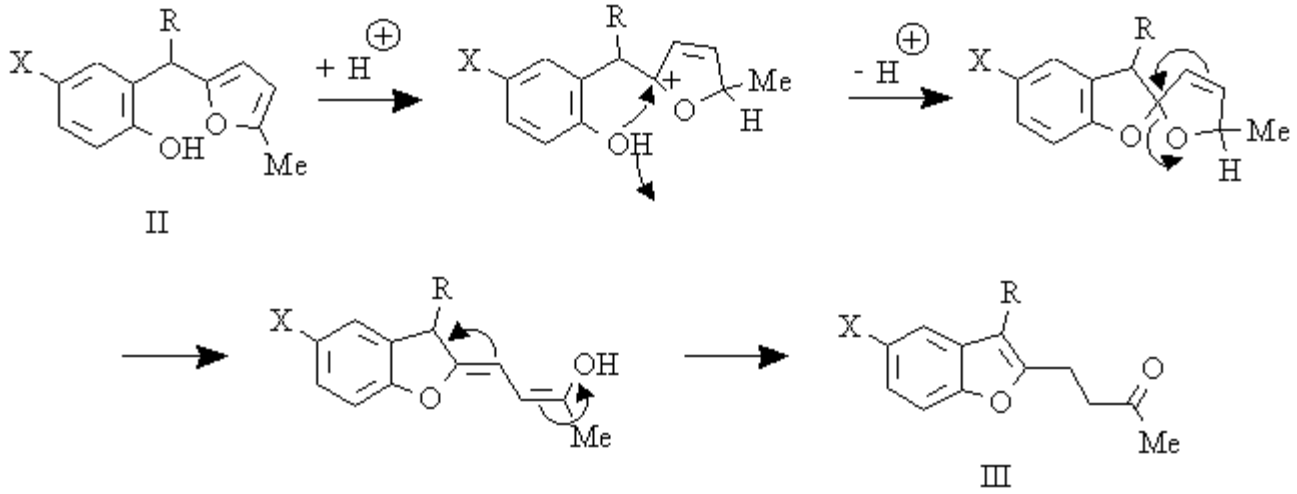


I II

IIa R=Ph, X=CH_3; IIb R=*p*-BrPh, X=CH_3; IIc R= *p*-CH_3Ph, X=CH_3; IId R=Ph, X=H; IIe R=*p*-CH_3Ph, X=H; IIf R=CH_2Ph, X=CH_3; IIg R=Et, X=CH_3.

At first time the reaction had been conducted in the presence of highly acid ion-exchanging resin Amberlyst-15 or boric acid in boiling benzene, but had never been completed. The best result was obtained with catalytic amount of p-toluenesulfonic acid and refluxing reagents in benzene solution with Dean-Stark trap that gave the corresponding methanes quantitatively.

The prepared methanes II easely transformed into benzofuran derivatives III under the treatment of ethanolic HCl solution according to the following scheme:

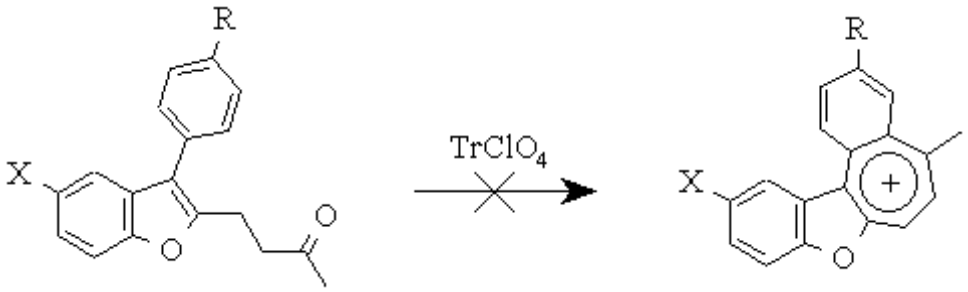


II

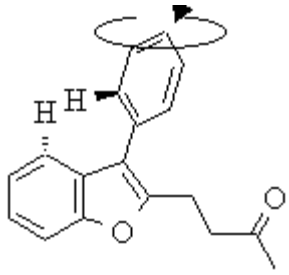
III

IIIa R=Ph, X=CH_3; IIIb R=*p*-BrPh, X=CH_3; IIIc R= *p*-CH_3Ph, X=CH_3; IIId R=Ph, X=H; IIIe R=*p*-CH_3Ph, X=H; IIIf R=CH_2Ph, X=CH_3; IIIg R=Et, X=CH_3.

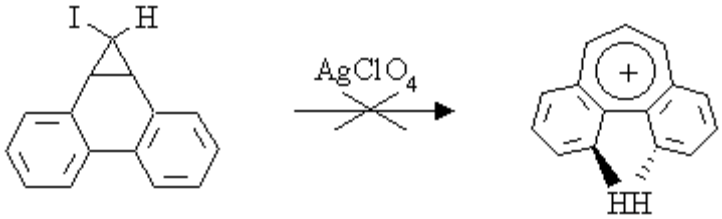
All attempts to carry out further oxidative cyclisation of prepared 3-arylbenzofurans III to appropriate dibenzoxazulenium cations using trityl perchlorate or chloranile/perchloric acid in boiling dioxane failed. Never signs of expected tetracyclic salts were discovered:



Such oxazulenium salts must to be aromatic, and cyclisation failed, to our opinion, not because of any electronic factors, but because of steric hindrance. Probably, the benzofuran proton in peri-position and o-proton of aryl ring mutually repulse that leads to twisting of aryl plane to benzofuran plane.

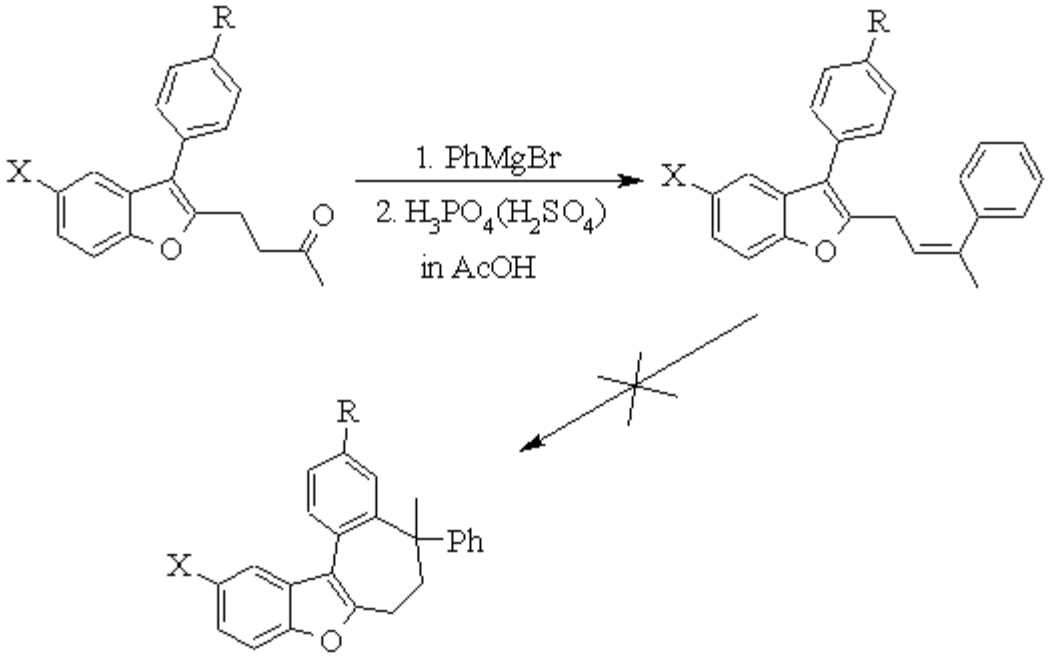


It`s known that dibenzo[a,c]tropilium cation was not obtained due to instability caused by repulsion between ortho-hydrogens excluding total complanarity of aromatic system[5]:



Green polymer was isolated despite of high stability of the cation that was predicted by MO LCAO. From another hand dibenz-[a,d]-tropilium salts are stable and well discribed compounds [6].

Our attempt to cyclize tertiary alkohol into oxazulene derivative according to the following scheme gave only the corresponding alkene, but not a tetracyclic oxazulene derivative.



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