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Quantum chemical evaluation of the yield of hydroxybenzophenones in the Fries rearrangement of hydroxyphenyl benzoates

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Abstract

The Fries rearrangement of resorcinol monobenzoate and orcinol monobenzoate was studied by using various molecular modelling approaches. The conformational analysis of the reactants and products was accomplished. The methods used were the molecular mechanical MM+ approach, the Hartree–Fock method with an STO-3G basis set and the density functional method B3LYP with basis sets 3-21G, 6-31G and 6-31+G*. The results obtained by using the B3LYP/6-31+G* method, unlike those obtained by using the lower-level methods, allowed calculation of the values of the thermodynamic distribution of isomeric components in equilibrium mixtures (monobenzoate/benzophenone) that appeared to be in good accordance with the experimental results.

Keywords: Resorcinol; Orcinol; Monobenzoate; Fries rearrangement; Polyhydroxybenzophenone; Conformational analysis; Ab initio calculations

1. Introduction

Benzophenones are compounds that efficiently absorb UV light. The benzophenone derivatives added to plastics, adhesives, etc. stabilize these materials to the UV light degradation [1].

2,4-Dihydroxybenzophenone (2,4-DHB) (**1**) (Scheme 1) is one of the valuable benzophenone products used, for instance, as an intermediate in the synthesis of 4-*O*-octyl-2-hydroxybenzophenone. The latter compound is useful as a UV radiation absorbent [1,2]. By using the Fries rearrangement of resorcinol monobenzoate (RMB) 2,4-DHB has been synthesized with good yield [1,2]. The synthesis started either from resorcinol and benzoic acid or the previously prepared RMB.

An objective of the present work was to evaluate possibilities of using 5-methylresorcinol as an alternative starting material to resorcinol for the synthesis of polyhydroxybenzophenones. This compound was investigated as the simplest representative of 5-alkylresorcinols produced annually in hundreds of metric tons when separating them from shale oil.

Good results have been obtained in the preparation of diarylketones by using the following synthetic strategies: the Fries rearrangement of arylbenzoates [3], the Friedel–Crafts acylations catalyzed by metal halides [4], and the oxidation of diarylmethanes [5,6]. The latter are readily prepared, for instance, by the Friedel–Crafts alkylation of phenols with benzyl alcohol [7–9]. For preliminary studies, we selected from these simple synthetic approaches the Fries rearrangement catalyzed by recoverable Brønsted acids (ion-exchange resins, etc.). The method seemed attractive as it is probably of the lowest environmental impact [10].

The Fries rearrangement of resorcinol monobenzoate (RMB) affording 2,4-DHB has been performed using different Brønsted acids [1,2,10] as well as Lewis acid catalysts (for example, $ZnCl_2$ [11]). For technological purposes, the former type of catalyst, especially heterogeneous recyclable medium- and large-pore zeolites [1,2,12–15] and ion-exchange resins in acid form—Amberlyst-15 and Nafion-H [1,2], is clearly preferable. When catalyzing the reaction of resorcinol with benzoic acid in 4-chlorotoluene at 162 °C (reflux) Amberlyst-15, in

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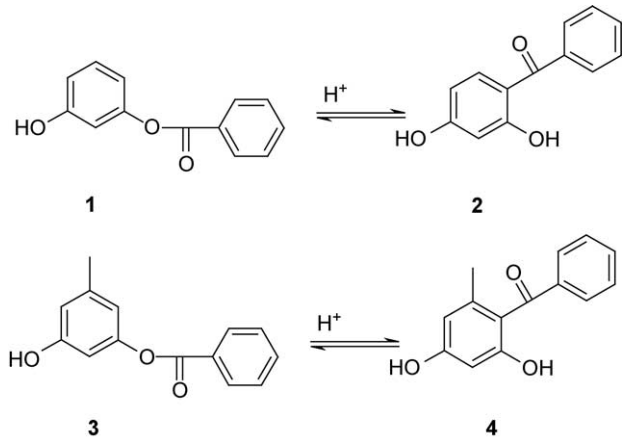


Scheme 1. The reversible Fries rearrangement of RMB (**1**) to 2,4-DHB (**2**) and of orcinol monobenzoate (**3**) to 2,4-dihydroxy-6-methylbenzophenone (**4**).

comparison with other catalysts, has given 2,4-DHB in satisfactory yield (59%) [1]. Upon treatment of resorcinol and benzoic acid under the same conditions using zeolite H-beta as a catalyst 2,4-DHB was obtained, in a 70% yield.

The Fries rearrangement has been shown to be a reversible reaction [16]. Despite several attempts, the exact mechanism of this reaction—whether it is an intra- or intermolecular reaction or both at the same time, has not yet fully been elucidated [2].

The Fries rearrangement has also been shown to be an equilibrium reaction. Heating aryl benzoates in 1,2-dichloroethane with trifluoromethanesulfonic acid as a catalyst at 170 °C for 1–3 days leads to equilibrium mixtures [17]. These results were further verified in the synthesis of 2,4-DHB [10]. Starting from an equimolar mixture of resorcinol and benzoic acid (with as well as without a solvent) and, in other experiments, from the above mixture with added RMB as well as from RMB alone, and heating these samples with an acid catalyst at 180 °C for 2 h led to the equilibrium mixtures consisting of 68.1–69.1% of 2,4-DHB and 30.9–31.9% of RMB [10].

In conclusion, the results cited above suggest that the acid-catalytic esterification of resorcinol with benzoic acid (at a high temperature), followed in situ by the Fries rearrangement of the RMB formed and yielding 2,4-DHB in a certain ratio to RMB, is a fully reversible process and evidently occurs under thermodynamic control.

Based on the above conclusion two equilibrium systems (Scheme 1) were investigated by using the conformational analysis of the reactants/products:

(1) RMB (**1**) and 2,4-DHB (**2**), and
(2) orcinol monobenzoate (**3**) and 2,4-dihydroxy-6-methylbenzophenone (**4**).

The reaction of orcinol monobenzoate was investigated experimentally as well (see Appendix A), while about

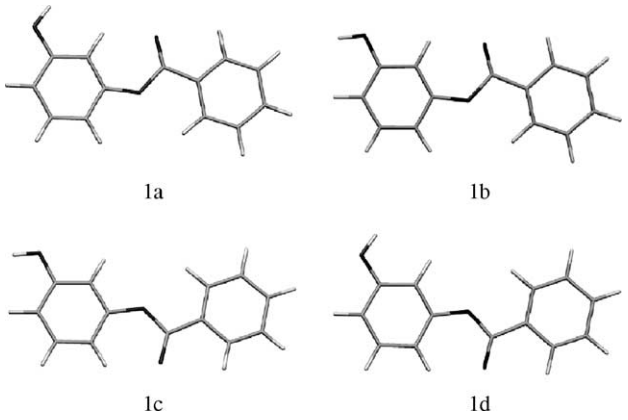


Fig. 1. Schematic structures of conformers of RMB (**1**) calculated at the level of B3LYP/6-31G.

the former system exhaustive factual material was found in the literature [1,2,10].

The aim of the current work was to show the possibility of making a theoretical evaluation of the yield of hydroxybenzophenones in the Fries rearrangement of hydroxyphenyl benzoates. We expected this yield to correspond to the thermodynamic distribution of isomers (benzophenone/benzoate in the above systems) at a certain temperature. The results of the conformational analysis corresponding to the gas phase were expected to describe the experimental situation occurring in any solvent (mesitylene, etc.) indifferent to the reactants.

As noted, another goal of the present work was to elucidate the usefulness of 5-alkylresorcinols (on an example of 5-methylresorcinol) for the synthesis of hydroxybenzophenones in the Fries rearrangement.

2. Conformational analysis, computational details

The software packages used were: HYPERCHEM (version 7.0) [18] and GAUSSIAN 98 (Rev. A.7.) [19].

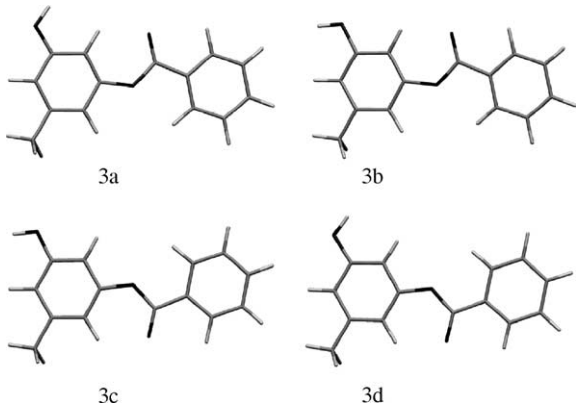


Fig. 2. Schematic structures of conformers of orcinol monobenzoate (**3**) calculated at the level of B3LYP/6-31G.

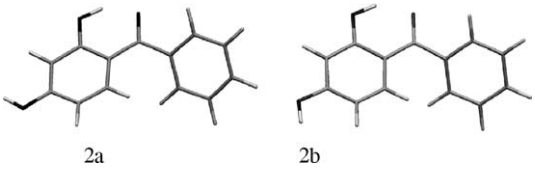


Fig. 3. Schematic structures of conformers of 2,4-DHB (**2**) calculated at the level of B3LYP/6-31G.

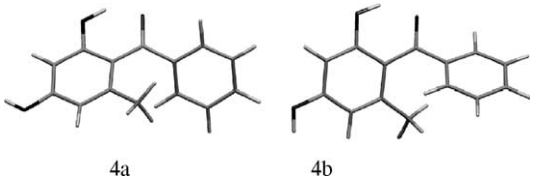


Fig. 4. Schematic structures of conformers of 2,4-dihydroxy-6-methyl-benzophenone (**4**) calculated at the level of B3LYP/6-31G.

2.1. The calculation procedure

In order to find all local energetic minima for molecules 1–4 (Scheme 1) the conformational landscape was explored with the help of the HYPERCHEM program using the MM+ force field [20]. This program allows generation of all possible conformers by varying different torsional angles. All the torsions significant in the conformational search were taken into account. The HYPERCHEM program minimizes the energy of each conformer generated and extracts the unique ones only.

All the HYPERCHEM-generated conformers were further calculated using the GAUSSIAN program with a full geometry optimization. In this step, the initial method was the Hartree–Fock method with an STO-3G basis set. These low-level ab initio calculated structures were, in turn, used as input structures for the density functional methods such as B3LYP [21] with a 3-21G basis set (B3LYP/3-21G). The output of the latter method was used as an input for the B3LYP/6-31G method. The optimization cascade was finalized using the same density functional method (B3LYP) with a 6-31+G* basis set.

Step-by-step, along with the optimization cascade, some of the generated (expected) conformers were converging on each other. As a result, the number of conformers to be optimized was substantially reduced according to each of the higher basis sets subsequently used. A schematic representation of the conformers of (**1**)–(**4**) based on the B3LYP/6-31G optimization are shown in Figs. 1–4.

3. Results and discussion

3.1. Conformational analysis

In Tables 1–4 relative energies (based on total energies) of conformers, as well as of isomers and their thermodynamic probabilities calculated by using the higher-level basis sets 6-31G and 6-31+G* are presented. The thermodynamic distribution of isomers (**1**)/(**2**) and (**3**)/(**4**) at a temperature of 140 °C was calculated according to Boltzman's law and is presented in Tables 1–4. The distribution of isomers (**1**)/(**2**) at 180 °C presented in Tables 1 and 2 was also calculated to allow comparison with literature data [10]. The results obtained have a qualitative value. Entropy changes were not taken into account. Nevertheless, the treatment above affords prolific results.

Table 1
Energies, conformer and compound ratio of isomers (**1**)–(**2**) (at a temperature of 140 °C) calculated using the method B3LYP/6-31G

Compound	Conformer	Energy (kcal/mol)	Conformer ratio	Compound ratio	Comformer ratio 2[a]	Compound ratio 2[a]
2	**a**	0.000	0.702	0.948	0.672	0.930
2	**b**	0.861	0.246		0.258	
1	**a**	2.746	0.025	0.052	0.032	0.070
1	**c**	3.477	0.010		0.014	
1	**d**	3.537	0.009		0.013	
1	**b**	3.670	0.008		0.011	
Sum			1.000	1.000	1.000	1.000

[a] Ratio 2 corresponds to a temperature of 180 °C.

Table 2
Energies, conformer and compound ratio of isomers (**1**)–(**2**) (at a temperature of 140 °C) calculated using the method B3LYP/6-31+G*

Compound	Conformer	Energy (kcal/mol)	Conformer ratio	Compound ratio	Conformer ratio 2[a]	Compound ratio 2[a]
2	**a**	0.000	0.465	0.701	0.445	0.685
2	**b**	0.555	0.237		0.240	
1	**a**	0.809	0.173	0.299	0.181	0.315
1	**b**	1.076	0.125		0.134	
Sum			1.000	1.000	1.000	1.000

[a] Ratio 2 corresponds to a temperature of 180 °C.

Table 3
Energies, conformer and compound ratio of isomers (**3**)–(**4**) (at a temperature of 140 °C) calculated using the method B3LYP/6-31G

Compound	Conformer	Energy (kcal/mol)	Conformer ratio	Compound ratio
3	**a**	0.000	0.464	0.992
3	**d**	0.719	0.193	
3	**c**	0.714	0.194	
3	**b**	0.981	0.140	
4	**a**	3.588	0.006	0.008
4	**b**	4.442	0.002	
Sum			1.000	1.000

Table 4
Energies, conformer and compound ratio of isomers (**3**)–(**4**) (at a temperature of 140 °C) calculated using the method B3LYP/6-31+G*

Compound	Conformer	Energy (kcal/mol)	Conformer ratio	Compound ratio
3	**a**	0.000	0.574	0.999
3	**b**	0.245	0.425	
4	**a**	5.512	0.001	
4	**b**	6.067	0.000	0.001
Sum			1.000	1.000

Table 5
The number of conformers remaining after the structure optimization using different methods

Structure	MM+	HF/STO-3G	B3LYP/3-21G	B3LYP/6-31G	B3LYP/6-31+G*
1	43	12	9	4	2
2	32	16	16	2	2
3	34	15	12	4	2
4	32	8	8	2	2

A general tendency in the conformational search is that higher-level methods significantly reduce the number of conformers. For example, in the case of structure (**1**), the HYPERCHEM MM+ method generated 43 conformers; after the geometry optimization with the HF/STO-3G method 12 unique structures still remained. B3LYP/3-21G and B3LYP/6-31G reduced the number of conformers to 9 and 5, respectively. The final optimization procedure, B3LYP/6-31+G*, reduced the number of conformers to two (Table 5).

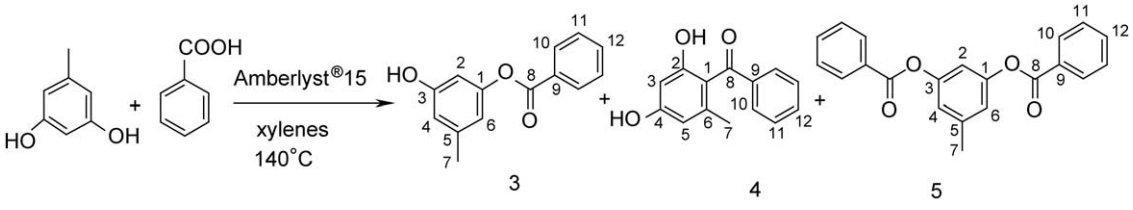
When replacing the basis set 6-31G by 6-31+G*, another important observation was the loss of the planarity of structures (**1**) and (**3**). In order to elucidate the latter important structural change the calculation of the reaction coordinate was performed changing the dihedral angle of C_8–O–C_1–C_2 (atom numbering is given in Scheme 2) from 0 to 180° with a step of 10° in structure (**1**). On each reaction coordinate point the full geometry optimization was performed. Such a reaction coordinate calculation is equivalent to the conformational change between structures (**1a**) and (**1d**) (Fig. 1).

The qualitative difference between these two reaction coordinate scans on different basis sets is shown in Figs. 5 and 6. In the case of a lower-level basis set there exist two structures with appropriate dihedral angles, 0 and 180°, with an energy difference of about 0.80 kcal/mol. In the case of a higher-level basis set the stable conformer has a dihedral angle of 50° and, obviously due to symmetry reasons, has another minimum at −50°. Thus, a double minimum seems to exist in this case and the energy barrier between these two minima is about 0.22 kcal/mol, which is very low.

A similar calculation was performed on structure (**3**) as well. The quantitative picture is very similar to that of structure (**1**) (Figs. 7 and 8).

The rotation of the O–H group was also performed. The appropriate dihedral angle was changed from 0 to 180°, with a step of 10°. In this scan there is no qualitative difference if the basis set 6-31G was replaced by 6-31+G*. Therefore, only structure (**1**) was investigated in such a way (Fig. 9).

In Figs. 10 and 11, minimum energy conformers for each compound investigated are shown. The addition of the CH_3 group to the hydroxyphenyl ring results in the change of the angle between two rings from 48.7 to 57.8° in case of compounds (**1**) and (**3**), and from 47.7 to 59.2° in case of compounds (**2**) and (**4**). This destabilizes especially structure (**4**) probably due to the lowering of both the conjugation as well as the hydrogen bond energy. There were great differences in the thermodynamic probability of conformers of the isomeric components of equilibrium mixtures (**1**)+(**2**) and (**3**)+(**4**) (Scheme 1), and in the corresponding thermodynamic distribution of isomers by using two higher basis sets— 6-31G and 6-31+G*. The former gives the thermodynamic distribution of 7.0/93.0 for isomers (**1**)/(**2**), while the latter gives a ratio of 31.5/68.5 for the same mixture (at a temperature of 180 °C).



Scheme 2. Acid-catalytic treatment of orcinol with benzoic acid.

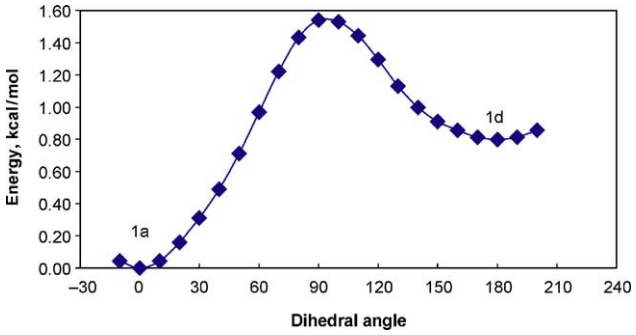


Fig. 5. A potential energy surface along the reaction coordinate between conformers (**1a**) and (**1d**) calculated with the B3LYP/6-31G method.

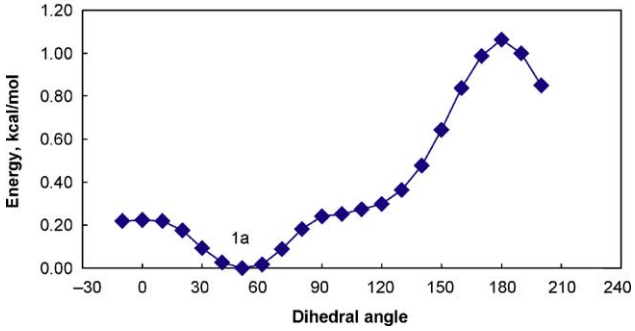


Fig. 6. A potential energy surface along the reaction coordinate between conformers (**1a**) and (**1d**) calculated with the B3LYP/6-31+G* method.

This appeared to be in good accordance with the experimental results (30.9–31.9/68.1–69.1) [10].

For mixture (**3**)+(**4**) (Scheme 1), the same basis sets gave different results. The ratio of 99.2/0.8 was obtained for isomers (**3**)/(**4**) using the B3LYP/6-31G method at a temperature of 140 °C. This is different from the equilibrium ratio of (**1**)/(**2**) as well as from the ratio of 99.9/0.1 obtained using the basis set 6-31+G*. However, these results are in good accordance with an experimental ratio of these isomers, ≈99.6/0.4.

In conclusion, the theoretical approach to the evaluation of the yield of hydroxybenzophenones in the Fries rearrangement of hydroxyphenyl benzoates presented

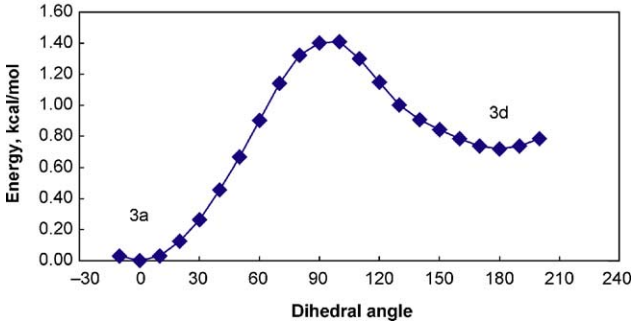


Fig. 7. A potential energy surface along the reaction coordinate between conformers (**3a**) and (**3d**) calculated with the B3LYP/6-31G method.

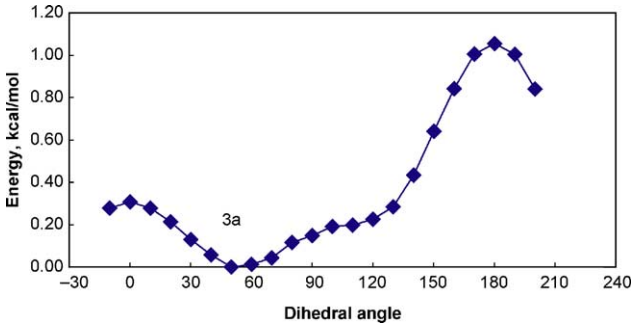


Fig. 8. A potential energy surface along the reaction coordinate between conformers (**3a**) and (**3d**) calculated with the B3LYP/6-31+G* method.

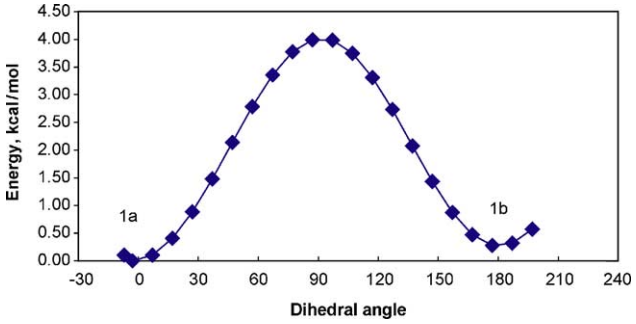


Fig. 9. A potential energy surface along the reaction coordinate between conformers (**1a**) and (**1b**) calculated with the B3LYP/6-31+G* method.

seems reliable considering the consistence of calculation and experimental results.

3.2. Experimental verification of the computational results

The esterification of orcinol with benzoic acid catalysed by Amberlyst-15 was performed in xylenes with an azeotropic removal of water (at 140 °C) from the system.

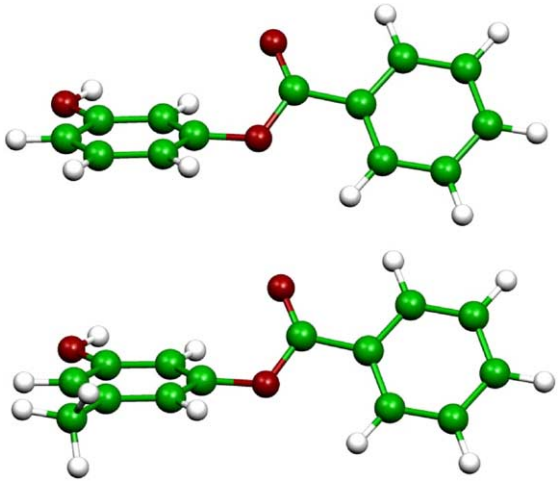


Fig. 10. Minimum energy conformers (**1a**) and (**3a**) optimized with the B3LYP/6-31+G* method.

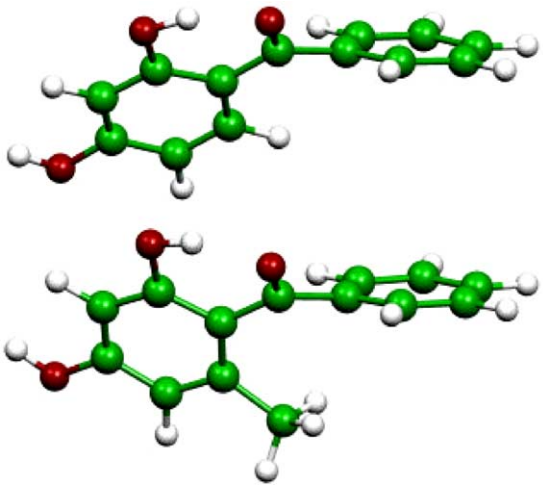


Fig. 11. Minimum energy conformers (**2a**) and (**4a**) optimized with the B3LYP/6-31+G* method.

The subsequent Fries rearrangement afforded only trace amounts of 2,4-dihydroxy-6-methylbenzophenone (in a 0.3% yield). Started from orcinol monobenzoate and orcinol dibenzoate the additional synthetic trials under the above conditions gave poor results as well. For another Fries rearrangement system studied in this work, RMB/2,4-DHB, the content of the equilibrium mixture (31.9–30.9/68.1–69.1) at 180 °C was reported in the literature [10].

The experimental is in good accordance with the theoretical results presented above.

4. Conclusions

1. In order to find an approach to the theoretical evaluation of the yield of hydroxybenzophenones in the Fries rearrangement of hydroxyphenyl benzoates, the conformational analysis of the components of two equilibrium reaction mixtures—resorcinol monobenzoate/2,4-dihydroxybenzophenone and orcinol monobenzoate/2,4-dihydroxy-6-methylbenzophenone was carried out by using the HYPERCHEM and GAUSSIAN software. The methods used were the molecular mechanical MM+ approach implemented in the HYPERCHEM program, the Hartree–Fock method with an STO-3G basis set and the density functional method B3LYP with basis sets 3-21G, 6-31G and 6-31+G*. The latter two methods are implemented in the GAUSSIAN program.
2. The results of the final geometry optimization of the generated conformers based on the B3LYP/6-31+G* method, unlike those obtained by using the lower-level methods, allowed calculation of the values of the thermodynamic distribution of isomeric components (monobenzoate/benzophenone) in the equilibrium reaction mixtures which are in good agreement with the experimental.
3. Based on the experimental results as well as on the quantum chemical evaluation it can be concluded that in the Fries rearrangement orcinol monobenzoate affords 2,4-dihydroxy-6-methylbenzophenone with a very low yield (<1%).

Acknowledgements

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Appendix A

A.1. Synthesis

A.1.1. General

The chemicals and solvents used were purchased from Merck and Aldrich. Amberlyst-15 was purchased from Fluka. Silica gel for column chromatography and TLC plates (foils 60 F254) were from Merck. The progress of the synthesis was monitored by TLC; the compounds were visualized by using anise aldehyde. ^{13}C and ^{1}H NMR spectra were recorded on a Bruker AMX-500 Spectrometer. The products were identified by performing the full assignment of ^{1}H and ^{13}C chemical shifts by using ^{1}H–^{1}H and ^{1}H–^{13}C 2D COSY correlation diagrams. UV spectra were taken on a Cary-50 UV–visible Spectrophotometer.

A.1.2. The acid-catalysed esterification/Fries rearrangement process starting from benzoic acid and 5-methylresorcinol

Orcinol monohydrate (2.84 g; 20 mmol) was dissolved in xylenes (150 ml; bp 138–142 °C), benzoic acid (2.440 g; 20 mmol) and Amberlyst-15 (1.42 g) were added. The reaction mixture was refluxed with azeotropic water isolation by using a Dean–Stark trap at 140 °C for 16 h. The reaction mixture was cooled, the catalyst filtered off and Et_2O (150 ml) added to the filtrate.

The resulting solution was washed with a saturated $NaHCO_3$ solution and brine, dried over Na_2SO_4 and filtered. The solution was evaporated on a rotary evaporator under reduced pressure to yield 4.24 g of crude product. The crude product was further fractionated by chromatography over silica gel (150 g, 40–100 μm) by eluting with solvent mixtures EtOAc/benzene (1/100→1/10). After evaporation the following fractions were obtained: (a) orcinol dibenzoate (**5**) 302 mg (yield 4.5%); (b) orcinol monobenzoate (**3**) 3.446 g (yield 75.5%); (c) 2,4-dihydroxy-6-methylbenzophenone (**4**) 14 mg (yield 0.3%); (d) (**4**) (trace)+orcinol 11 mg; (e) orcinol: 287 mg (11.6%).

Characteristics of the products: ^{13}C NMR chem. shifts δ ($CDCl_3$; the numbering of carbon atoms of the molecules is

presented in Scheme 2): (**3**) C_1 151.3; C_2 106.4; C_3 156.6; C_4 114.2; C_5 140.7; C_6 114.2; C_7 21.3; C_8 165.9; C_9 129.3; C_{10} 130.2; C_{11} 128.6; C_{12} 133.7; (**4**) C_1 115.8; C_2 163.2; C_3 101.3; C_4 160.7; C_5 111.3; C_6 141.0; C_7 23.4; C_8 201.3; C_9 142.4; C_{10} 128.4; C_{11} 128.6; C_{12} 132.2; (**5**) C_1 151.1; C_2 119.9; C_3 151.1; C_4 112.7; C_5 140.5; C_6 112.7; C_7 21.4; C_8 164.8; C_9 129.3; C_{10} 130.1; C_{11} 128.5; C_{12} 133.6.

TLC: R_f=(**3**) 0.51; (**4**) 0.35; (**5**) 0.7 (eluent: benzene/ethyl acetate 10/1).

UV: (**3**) λ_{max}=227.9 nm (ε=18,590; MeOH); (**4**) λ_{max}=249.4 nm (ε=17,800; MeOH).

The experimental ratio of isomers (**3**)/(**4**) in the equilibrium mixture at 140 °C was found to be ≈99.6/0.4.

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