

# Regio- and Stereoselectivity in the Paternò-Büchi Reaction on Furan Derivatives

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The photochemical coupling reaction between 2,3-dihydrofuran and benzaldehyde was studied by using DFT/B3LYP/6-31G+(*d,p*) method. The regiocontrol of the attack of the benzaldehyde on the double bond is related to the different stabilities of the biradical intermediates. The *endo* stereoselectivity of the reaction depends on the superposition between HSOMO and LSOMO in the biradical intermediate. In the photochemical reaction between furan and benzaldehyde also the regiocontrol depends on the relative stability of the possible biradical intermediates. The *exo* stereoselectivity of the coupling reaction depends on the superposition between the HSOMO and LSOMO of the biradical intermediate. The reaction of chiral phenylglyoxylates with furan gave the corresponding adducts with *de* = 15–95%. The stereocontrol can be explained considering the energy gap between the biradical intermediates in the coupling reaction. When the reaction was performed in the presence of zeolite, the diastereoisomeric excess increased. The reaction of benzoin and 2-phenylpropiophenone with furan gave the cycloadduct with high diastereoselectivity. All the products were obtained with *de* > 98%. The Paternò-Büchi reaction between 2-furylmethanols with aromatic carbonyl compounds also showed high regio- and stereocontrol. On the contrary, when 5-methyl derivatives were used, a lack of regiocontrol was observed. Furthermore, with aliphatic carbonyl compounds, no diastereoselectivity was observed. These results were explained assuming the attack of the excited carbonyl compound on the same side as the hydroxyl group, through the formation of a hydrogen bond or of a complex. This type of attack gave the biradical intermediate in preferential conformations. The relative energies of these conformers account for the observed diastereoselectivity.

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## 1. INTRODUCTION

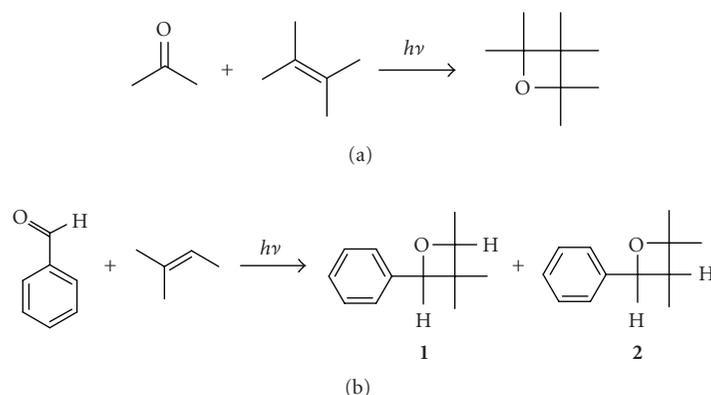
[2 + 2]-cycloadditions are one of the most important reactions in organic photochemistry. Several applications in organic synthesis have been described [1]. The Paternò-Büchi reaction is a [2 + 2]-cycloaddition reaction between a carbonyl compound and an alkene (Scheme 1(a)). The regiochemistry of this reaction appeared to be a difficult problem to solve from the first. Paternò performed a reaction between 2-methyl-2-butene and benzaldehyde, and he could not assign the exact structure of the product. He was not able to distinguish between **1** and **2** (Scheme 1(b)) [2]. Büchi solved the problem showing that **1** was the actual product [3]. Furthermore, in this reaction the stereocontrol was not examined, but several stereoisomers could be obtained.

Regio- and stereocontrol of the Paternò-Büchi reaction was not always understood. For several years the comprehension level of these two factors resembled the description of some problems connected with the evolution of photo-

chemistry made by Ciamician in 1912: “in ordinary organic chemistry the reactions often take place in some definite way; but the photochemical reactions often furnish surprises and proceed along quite different lines” [4].

The Paternò-Büchi reaction is a photocycloaddition of an *n, π\** carbonyl compound in either its *S*<sub>1</sub> or the *T*<sub>1</sub> state to an alkene in its ground state. In a theoretical study the authors showed that there are two conical intersection points located near the C–C and C–O bonded biradical regions of the ground state [5]. Furthermore, for C–O attack, the triplet surface must cross the singlet to reach a diradicaloid minimum.

For C–C attack, the triplet state biradical minimum is located at the same geometry as the conical intersection between the two singlet states, and the efficiency of the intersystem crossing will be determined by the nature of the spin-orbit coupling. Thus, for the triplet, the reaction path can be predicted by the most stable biradical rule [5]. The biradical intermediate in the reaction between benzophenone



SCHEME 1

and electron-rich alkenes has been determined by using laser flash photolysis [6, 7]. A conformational analysis of the biradicals has been published [8].

Furan derivatives can give the Paternò-Büchi reaction reacting with carbonyl compounds. This reaction has been used extensively in the synthesis of natural products [9, 10].

In order to explain both regio- and stereocontrol of the Paternò-Büchi reaction on furan derivatives, we used the pattern represented in the Scheme 2 on the basis of the work of Scharf [11]. We assumed that the formation of the possible biradicals is reversible. The consequence of this hypothesis is, in agreement with the theoretical study, that the formation of the more stable intermediate is preferred, while all the other isomers undergo retrocleavage. The following ring closure is an irreversible step, determined by spin-orbit coupling [12–14], that usually allowed the formation of the more stable compound [15].

Obviously, in the presence of achiral precursors,  $k_1 = k_2$  as well as  $k_3 = k_4$ . In the presence of chiral reagents or in a chiral environment, we can observe  $k_1 \neq k_2$  and  $k_3 \neq k_4$ .

## 2. THE PATERNÒ-BÜCHI REACTION ON FURAN DERIVATIVES

### 2.1. 2,3-dihydrofurans

The irradiation of 2,3-dihydrofuran (**3**) with benzophenone gave the head-to-tail adduct **4** [16]. The same behaviour was observed irradiating 2,3-dihydrofuran with aliphatic aldehydes or ketones. By using acetone the adducts were obtained in a 200 : 1 isomeric ratio [17].

When benzaldehyde was used as carbonyl compound, the adducts were obtained as a > 98 : 2 regioisomeric mixture. The major isomer is 88 : 12 *endo/exo* mixture (Scheme 3). The reaction showed a good regio- and stereoselectivity [18–20]. Benzaldehyde reacts in its triplet state. A triplet biradical is formed as an intermediate.

We examined the regiochemistry of the reaction, and we tested the possibility that the regiochemical behaviour of the reaction is determined by the formation of the more stable biradical intermediate. We performed DFT/B3LYP calcula-

tions using 6-31G + (*d, p*) basis set on Gaussian 03. We examined the structures **M** and **N** (Figure 1).

The biradical **N** is more stable than **M** by 1.49 kcal mol<sup>-1</sup>. This result is in agreement with the experimental result. On the basis of this result the stability of the biradical intermediates can account for the regiochemical behaviour of the reaction.

We can see also why the *endo* isomer is favoured in the reaction. In Figure 2 we have depicted the HSOMO and the LSOMO of the biradical **N**. The HSOMO is mainly localized on the aromatic ring and it is extended on the benzylic radical site. The LSOMO is mainly localized on the dihydrofuran ring. The coupling between the radical carbons in these two orbitals is possible (the atomic orbitals involved can superimpose themselves) only if the *endo* isomer is formed (Figure 3).

### 2.2. Furans

#### 2.2.1. Photoaddition of benzaldehyde and benzophenone

Schenk reported that the irradiation of benzophenone in furan gave the head-to-head adduct in 94% yield [21, 22]. The analogous photoadduct **6** of benzaldehyde to furan (**5**) [23] has the 6-*exo* configuration as confirmed by NOE analysis (Scheme 4) [24, 25].

We also examined for this case the regioisomeric biradical intermediates **O** and **P** resulting from the head-to-head and the head-to-tail addition, respectively (Figure 4).

The biradical **O** is more stable than **P** by 16.5 kcal mol<sup>-1</sup>. The biradical **O** exists as two conformers and we considered only that conformer able to give the ring closure. The HSOMO and LSOMO of the biradical **O** are reported in Figure 5.

Also in this case the HSOMO is mainly localized on the benzaldehyde fragment of the biradical while the LSOMO is mainly localized on the furanoid part of the molecule. The coupling between the radical carbons in these two orbitals, considering that the atomic orbitals involved can superimpose themselves, can give only the *exo* isomer, in agreement with the experimental results (Figure 6).

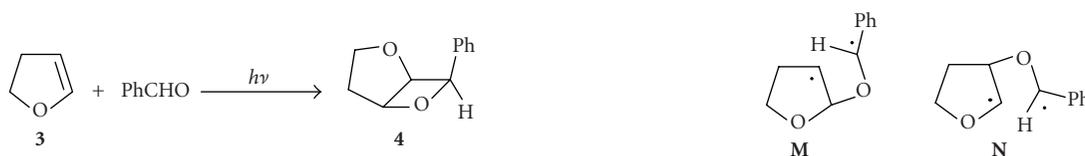
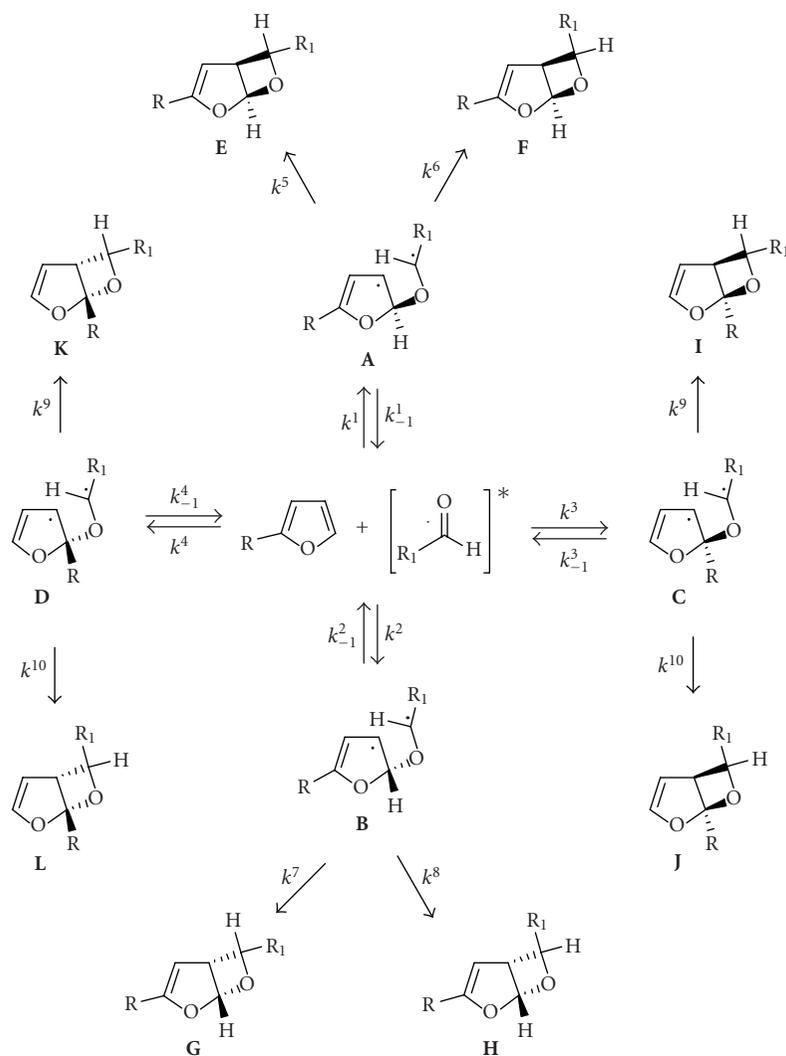


FIGURE 1: Possible biradical intermediates in the reaction of 2,3-dihydrofuran with benzaldehyde.

### 2.2.2. Photoaddition of chiral carboxyl compounds to furans

We studied the photocycloaddition of three enantiopure phenylglyoxylates, namely, compound **7**, obtained from (*S*)-1-methyl-1-propanol, compound **8**, obtained from (*S*)-2-methyl-1-butanol, and compound **9**, obtained from (-)-8-phenylmenthol (Figure 7) [26].

All the reactions gave in good yields the corresponding oxetanes. Considering the stereocontrol of the reaction, while the reaction with 8-phenylmenthol glyoxylate gave a high di-

astereoisomeric excess, the reaction with the glyoxylate ester **7** gave only 15% de and the reaction with the glyoxylate ester **8** resulted in no diastereoselectivity (Figure 7).

The best results in order to justify the observed stereoselectivity can be obtained considering the energy of the triplet biradical intermediates in the reaction of **7–9** with furan (Figure 8).

Calculations on these biradical intermediates showed that **Qa** (the precursor of **10**) was more stable than **Qb** by

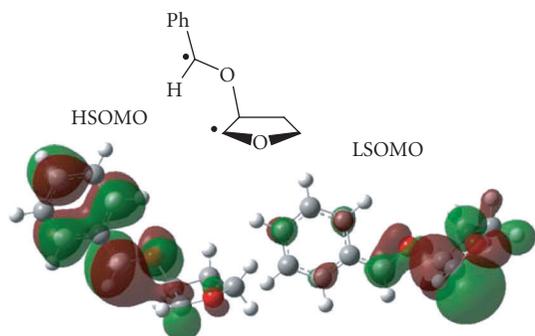


FIGURE 2: HSOMO and LSOMO of the biradical intermediate **N**.

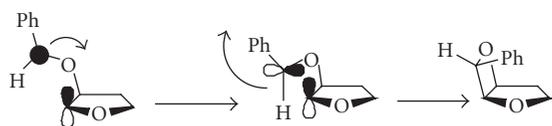
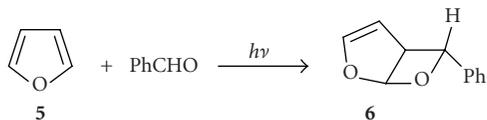


FIGURE 3: Ring-closure reaction in the formation of the *endo* isomer of the adduct between 2,3-dihydrofuran and benzaldehyde.



SCHEME 4

0.73 kcal mol<sup>-1</sup>. Furthermore, **Ra** and **Rb** differed by only 0.02 kcal mol<sup>-1</sup>, in agreement with the observed lack of stereoselectivity of the reaction. Finally, the biradical intermediate **Sa** showed to be more stable than **Sb** by 21.9 kcal mol<sup>-1</sup>: also this result is in agreement with the observed high diastereoisomeric excess.

In conclusion, the stereocontrol of the Paternò-Büchi reaction between **7–9** and furan can be explained considering the relative stability of the possible biradical intermediates.

To improve diastereoselectivity, we tried to carry out a reaction in an organized medium (zeolite). Selective absorption on the surface of the solid (NaY) could improve diastereoselectivity. We obtained the adducts **10–12**. It is noteworthy that this type of procedure allowed us to improve diastereoselectivity: while, in the reaction in solution, **10** was obtained with *de* = 15%, the reaction in an organized medium gave *de* = 37%. While **11** was obtained as a mixture of diastereoisomers, the use of the zeolite allowed to reach 18% diastereoisomeric excess. Also in the case of **12**, obtained in solution with *de* = 95%, the use of the zeolite increases the diastereoisomeric excess reaching the value of 98%.

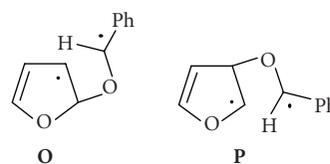


FIGURE 4: Possible biradical intermediates in the reaction of furan with benzaldehyde.

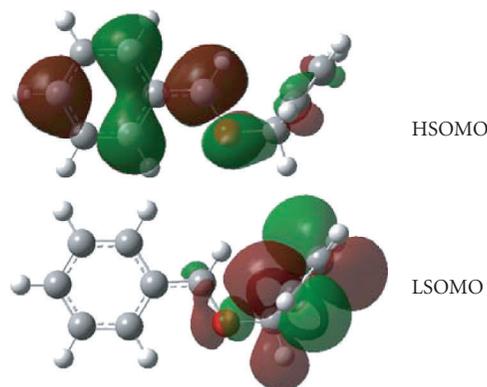


FIGURE 5: HSOMO and LSOMO of biradical intermediate **O**.

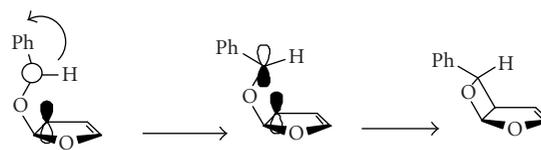


FIGURE 6: Ring-closure reaction in the formation of the *exo* isomer of the adduct between furan and benzaldehyde.

If the chiral center is near the reaction site, the diastereoselectivity increases. Benzoin (**13**) reacted with furan to give the corresponding adduct **14** in acceptable yield (56%) and *de* > 98% (Figure 9) [27].

Also in this case we calculated the energy of the intermediates **Ta** and **Tb** for the reaction of benzoin with furan. The structures are depicted in Figure 10. The biradical **Ta** was more stable than **Tb** for 3.66 kcal mol<sup>-1</sup>, in agreement with the observed stereoselectivity.

When chiral ketones were used as substrates we obtained products deriving from the Norrish Type II reaction. In order to avoid Norrish Type II reaction we used a substrate without  $\gamma$ -hydrogen. We used the phenyl derivative **16** (Figure 11). In this case we observed the formation of the corresponding adduct [28].

The NMR data for the compound **16** are in agreement for an *exo* position for the phenyl group at C-6. Chiral HPLC (Chiralcel OJ,  $\lambda$  = 235 nm, 99 : 1 *n*-hexane/isopropanol) showed a *de* > 98%.

We calculated the total energy of the possible intermediates in the reaction of **15** with furan. The structures of these compounds (**Ua**, **1Ub**) are showed in Figure 12.

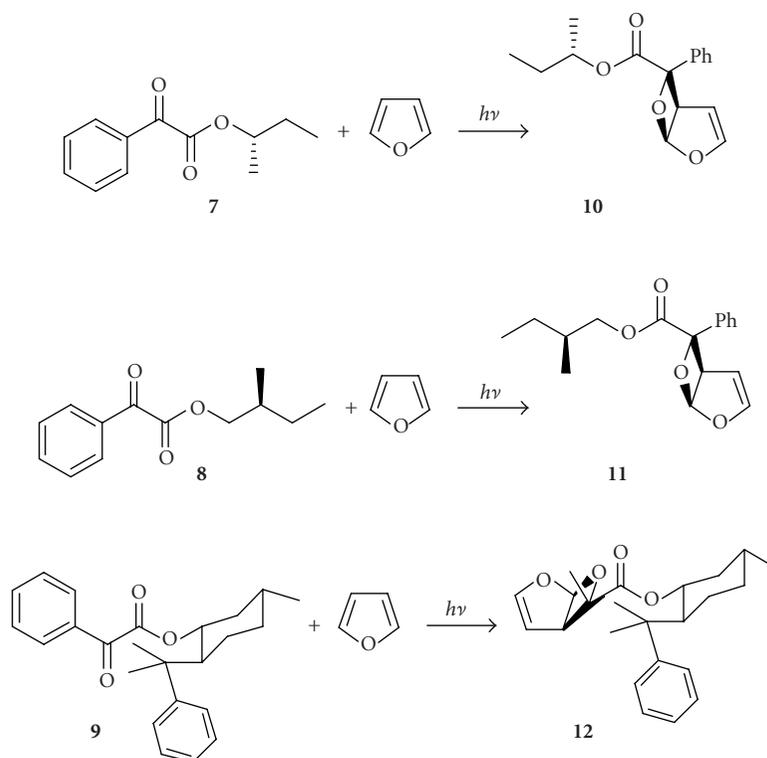


FIGURE 7: The reaction of chiral phenylglyoxylates with furan.

The *R,S* conformer **Ub** is more stable than the *S,S* one by  $1.1 \text{ kcal mol}^{-1}$  and this difference can account for the observed diastereoselectivity.

Furthermore, the analysis of the HSOMO and LSOMO in this biradical intermediate (Figure 13) shows that the coupling can occur to give the product with the phenyl group in the *exo* configuration.

### 2.2.3. Photoaddition of carbonyl compounds to chiral furans

The diastereoselectivity of the Paternò-Büchi reaction can be determined in the presence of some substituents, that is, the presence of chiral substituents on the alkene. Adam showed that allylic alcohols **17** reacted with benzophenone to give the corresponding adducts **18** and **19** with high region- and diastereoselectivity (Scheme 5) [29–32].

The diastereoselectivity dropped drastically in the presence of the protic solvent methanol and totally disappeared for the corresponding silyl ethers. These data are in agreement with the presence of a hydroxyl directing effect in the Paternò-Büchi reaction. The *threo* isomer can be favoured through the formation of a hydrogen bond between triplet excited benzophenone and the substrate in the exciplex, while the formation of the *erythro* stereoisomer would be less favoured due to allylic strain (Scheme 6).

The formation of a hydrogen bond directing the Paternò-Büchi reaction has been considered by other researchers.

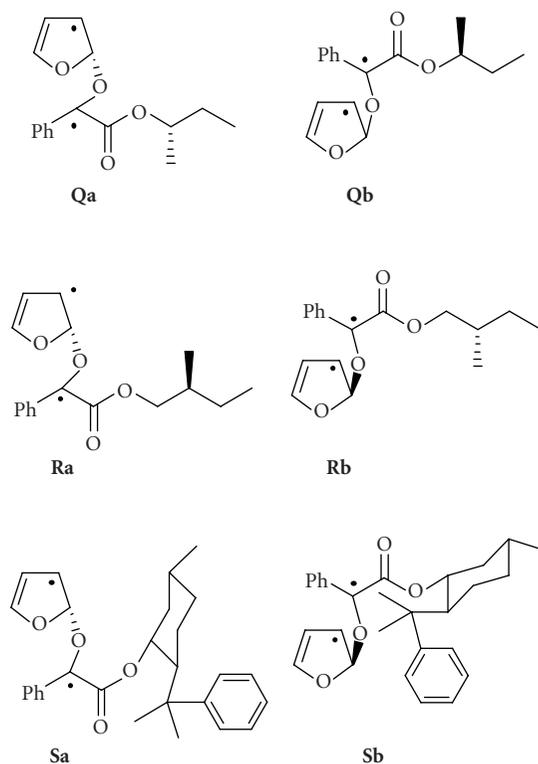


FIGURE 8: Radical intermediates in the reaction of 7–9 with furan.

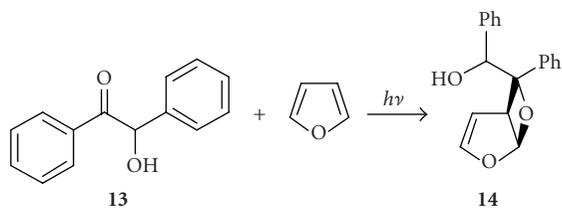


FIGURE 9: Photochemical reaction between benzoin and furan.

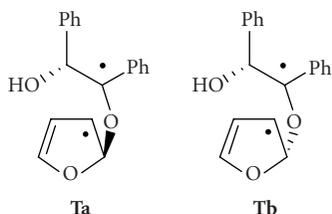


FIGURE 10: Biradical intermediates in the reaction of benzoin with furan.

Diastereoselective cycloaddition has been obtained using chiral enamide [33, 34], or in the reaction of allylic alcohols with naphthalene rings [35]. When unsymmetrical carbonyl partners such as acetophenone or benzaldehyde were used, high diastereoselectivity was observed to give the corresponding *cis* isomer. The regioselectivity was high with acetophenone but lower with benzaldehyde [30].

*Cis* diastereoselectivity can be explained by using the Griesbeck rule on the possible triplet biradicals formed in the reaction. Steric interactions are minimized when the biradical assumes the optimal conformation and this conformation accounts for the formation of the observed stereoisomer [32].

When chiral allylic alcohols were used as substrates in the reaction, *cis* diastereoisomers were formed. Also in this case, a pronounced *threo* diastereoselectivity was observed, in agreement with a less pronounced hydroxyl directing effect when acetophenone and benzaldehyde were used [30, 32]. A chiral allyl ether gave the corresponding adduct with high diastereoselectivity [36].

The reaction of allylic alcohols with carbonyl compounds was tested also on a particular type of allylic alcohol such as 2-furylmethanol derivatives. While the reaction of 2-furylmethanol with benzophenone showed low regioselectivity, the presence of larger substituents on the carbon bearing the alcoholic function allows a high regioselectivity (Scheme 7) [37]. Furthermore, when 2-furylethanol (**20**) was used as substrate, a 1 : 1 mixture of stereoisomers was obtained, while, when 1-(2-furyl)-benzylic alcohol (**21**) was the substrate, only one diastereoisomer was obtained. The high diastereoselectivity observed was confirmed using optically active **21**.

The regioselectivity of the reaction was explained on the basis of the relative stability of the biradical intermediates. A theoretical study (DFT) showed that the biradical obtained

on the most hindered side of the molecule was more stable than the other [38]. The nature of the intermediate was in agreement with the observed  $\rho$  value in a Hammett free energy correlation.

When 5-methyl-2-furyl derivatives were used as substrates, a different regioselectivity was observed. Compound **22** gave a 1 : 1 mixture of regioisomers **25** and **26**, when irradiated in the presence of benzophenone, and a single regioisomer **27** in the presence of benzaldehyde on the side bearing the methyl group (Scheme 7) [38]. In agreement with the results obtained with 2-furyl derivatives, the products deriving from the attack on the side bearing the alcoholic function were obtained as a single diastereoisomer, while those deriving from the attack on the side bearing the methyl group were obtained as a mixture of diastereoisomers. Then, the hydroxyl group near the reaction center is needed to have diastereoselectivity.

The reaction of 2-furylmethanol derivatives with aliphatic aldehydes and ketones gave the corresponding adducts with high regioselectivity but no diastereoselectivity (Scheme 7) [39].

The observed diastereoselectivity in the reaction with aromatic carbonyl compounds clearly shows that it increases in relation to the nature of the substituents on the carbon bearing the alcoholic function as described by Adam. However, while Adam considers the allylic strain with a methyl group as the driving force for the diastereoselectivity [29–31], in this case, the methyl group is not present. Therefore, the allylic strain cannot be used to explain diastereoselectivity.

In order to have more data to explain the observed stereoselectivity we studied the photochemical behaviour of tertiary 2-furylcarbinols [40]. The photochemical reaction of 1-methyl-1-phenyl-1-(2-furyl)methanol **28** with benzaldehyde gave a mixture of two regioisomeric products **29** and **30**.

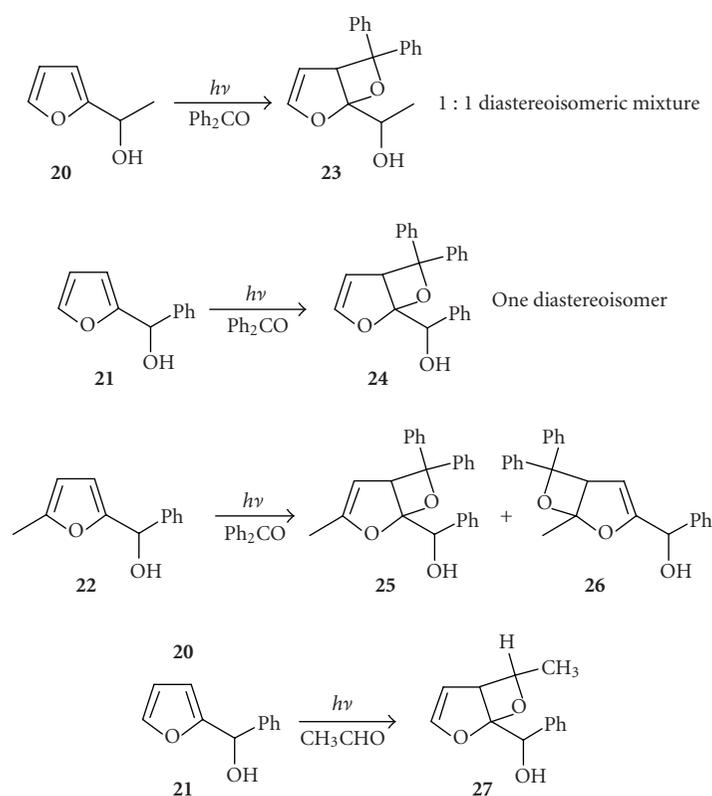
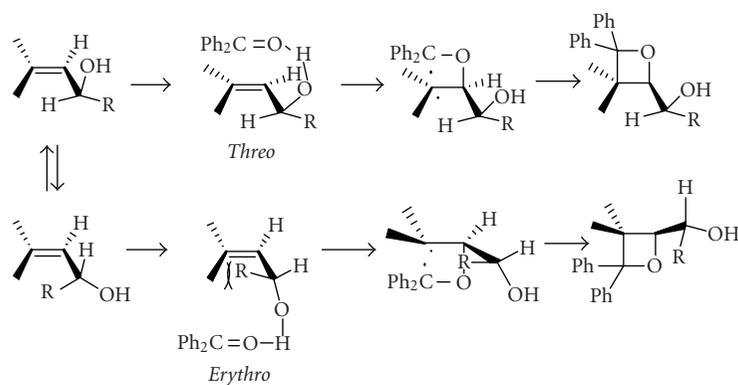
The regioisomer on the most hindered side of the molecule was obtained in low yield but it showed a complete diastereoisomeric control. On the contrary the main product was a mixture of four diastereoisomeric products (Scheme 8). The reaction of the same compound **28** with benzophenone gave only the product deriving from the attack on the most hindered double bond of molecule **31**. This compound was obtained with 48% diastereoisomeric excess.

The reaction of 1-methyl-1-*t*-butyl-1-(2-furyl)methanol (**32**) with benzaldehyde and benzophenone showed complete regioselectivity. In all the experiments only the products deriving from the attack of the carbonyl compound on the most hindered double bond of the substrate were observed (Scheme 9).

The regiocontrol was explained, as described above, considering the relative stability of the biradical intermediates. In this case, in the reaction of the 1-methyl-1-phenyl-1-(2-furyl)methanol with benzaldehyde the biradical obtained from attack on the less hindered double bond of the substrate was more stable than the other one by 18.03 kJ mol<sup>-1</sup>.

On the basis of these results we can attempt an explanation of the stereocontrol. 1-Methyl-1-phenyl-1-(2-furyl)methanol may exist in three conformations (Figure 14). All



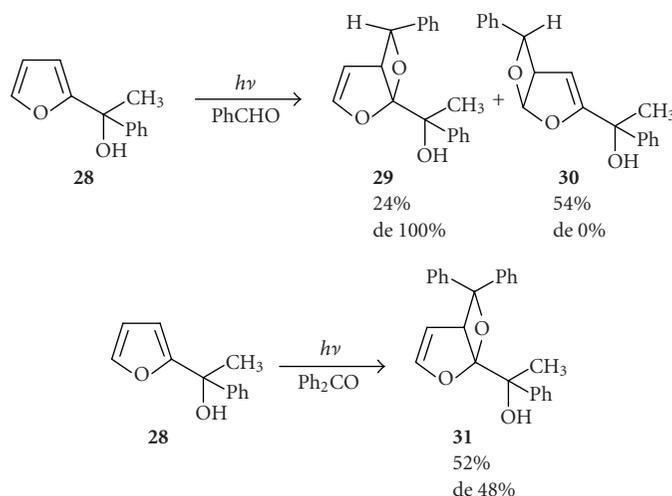


biradical. The conformer **AL** is more stable than **AI** by  $16.57 \text{ kJ mol}^{-1}$ , in agreement with the observed high diastereoselectivity. Furthermore, the same compound reacted with acetone to give the corresponding adduct without diastereoselectivity. Also in this case conformers **AI** and **AL** are those showing lowest energy but the difference between them is  $1.09 \text{ kJ mol}^{-1}$ , in agreement with the observed lack of diastereoselectivity.

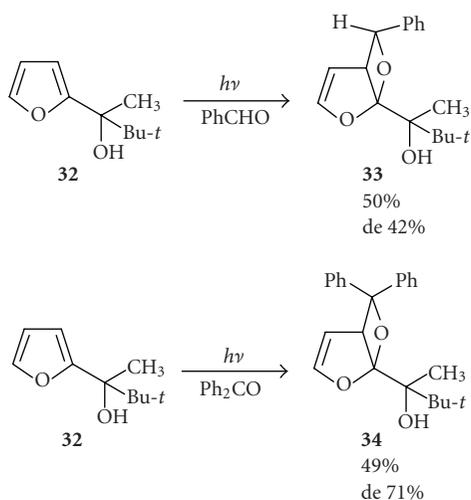
The same approach can be used to justify the stereocontrol of the reaction of allylic alcohols with benzophenone [41].

### 3. CONCLUSION

In conclusion we have shown that the regiocontrol of the attack of the benzaldehyde on the double bond is related to the different stability of the biradical intermediates. The *endo* stereoselectivity of the reaction depends on the superposition between HSOMO and LSOMO in the biradical intermediate. The regiocontrol depends on the relative stability of the possible biradical intermediates. The *exo* stereoselectivity of the coupling reaction depends on the superposition between the HSOMO and LSOMO of the biradical intermediate.



SCHEME 8



SCHEME 9

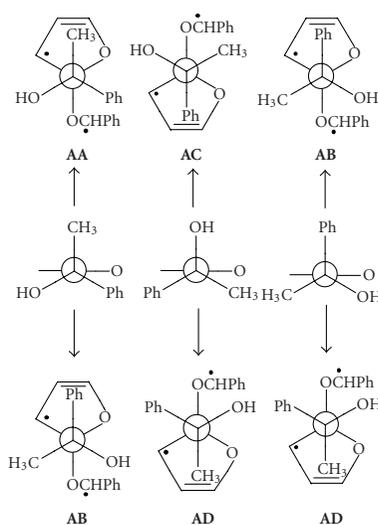


FIGURE 14: Possible conformations of the biradical intermediate from the reaction of 1-methyl-1-phenyl-1-(2-furyl)methanol with benzaldehyde.

The stereocontrol in the reaction between furan and chiral phenylglyoxylates can be explained considering the energy gap between the biradical intermediates in the coupling reaction. When the reaction was performed in the presence of zeolite, the diastereoisomeric excess increased. The reaction of benzoin and 2-phenylpropiophenone with furan gave the corresponding adduct with high diastereoselectivity.

The Paternò-Büchi reaction between 2-furylmethanols with aromatic carbonyl compounds showed high regio- and stereocontrol. The results were explained assuming the attack of the excited carbonyl compound on the same side as the hydroxyl group, through the formation of a hydrogen bond or of a complex. This type of attack gave the biradical intermediate in preferred conformations. The relative energies of these conformers account for the observed diastereoselectivity.

The above-reported discussion of the state of art points out some arguments that can be the object of future work in

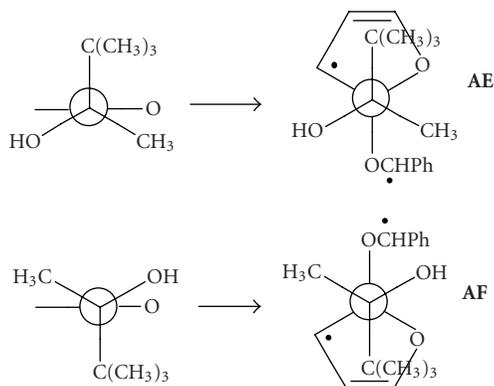


FIGURE 15: Possible conformations of the biradical intermediate from the reaction of 1-methyl-1-phenyl-1-(2-furyl)methanol with benzaldehyde.

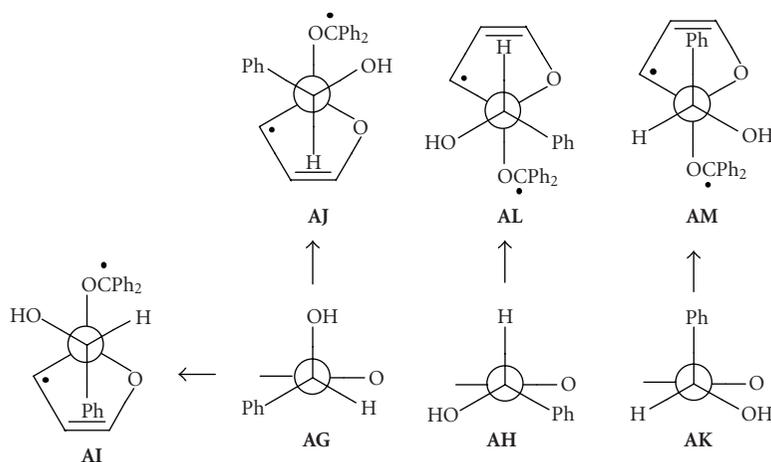


FIGURE 16: Possible conformations of the biradical intermediate from the reaction of 2-furylphenylmethanol with benzophenone.

this field: some hypotheses able to explain the simple stereoselectivity observed in the reaction between furan and benzaldehyde have been reported. This selectivity has to be confirmed studying the photochemical behavior of other carbonyl compounds, in particular heterocyclic carbonyl compounds. We have only very few data on furan- and thiophene-2-carbaldehyde [42–44]. In particular, the possible role of the excited singlet state in this reaction has to be explained, and some heterocyclic aldehydes have a long half-life.

Diastereoselective synthesis has been performed by using chiral substrates. It is not clear if this behaviour is a general character of this reaction: we need to test this behavior on a large number of chiral ketones.

High stereoselectivity was observed in the reaction between 2-furylphenylmethanol derivatives and carbonyl compounds. We do not know the photochemical behaviour of 3-furylphenylmethanol derivatives.

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