

## Regio- and stereoselectivity in the Paternò–Büchi reaction on furan derivatives

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### Abstract

The regiochemistry of the attack of a carbonyl group on furan, 2,3-dihydrofuran, 2-methylfuran, and 2-furylmethanol was explained assuming a frontier orbitals control of the reaction. The preferential formation of the *endo* adduct in the reaction between 2,3-dihydrofuran and benzaldehyde and the preferential formation of the *exo* isomer in the reaction between furan and benzaldehyde were explained considering the relative stability of the adducts. In the case of 2-methylfuran, the reaction with benzaldehyde gave the product deriving from the attack on the less hindered side of the molecule. The regiochemistry was explained considering the relative stability of the possible biradical intermediates. The *exo* stereoselectivity was explained on the basis of the stability of the adducts. 2-Furylmethanol gave a mixture of regioisomeric products where the most abundant one was that deriving from the attack on the most hindered side of the molecule. The regioselectivity was explained on the basis of the relative stability of the biradical intermediates.

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**Keywords:** Stereoselectivity; Paternò–Büchi reaction; Furan derivatives; Regiochemistry

### 1. Introduction

The Paternò–Büchi reaction is a milestone in organic photochemistry [1,2]. Several reviews cover the enormous number of papers published in this field [3–7]. The Paternò–Büchi reaction is a photocycloaddition of a  $n,\pi^*$  carbonyl compound to an alkene in the ground state from either the  $S_1$  or the  $T_1$  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. Furthermore, for C–O attack, the triplet surface must cross the singlet to reach a diradicaloid minimum. For C–C attack, the triplet 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 [8]. The biradical intermediate in the reaction between benzophenone and electron-rich alkene has been determined by using laser flash photolysis [9,10].

When the reaction is carried out on furan derivatives, it shows a good regio- and stereoselectivity (see below).

Several explanations of this behavior have been formulated. However, no explanation allows us to predict the stereochemical behavior of a Paternò–Büchi reaction.

In order to explain the observed diastereoselectivity in the reaction of furan with chiral phenylglyoxylic esters, Scharf proposed the following scheme (Scheme 1) [11].

For the weighting of the rate constants  $k_1$  and  $k'_{-1}$  on the one hand, and  $k_1/k_{-1}$  or  $k'_2/k'_{-1}$  on the other, two boundary cases can be discussed in the above-reported model: (1) the intermediate formed preferentially can also react preferentially to give the product (Fig. 1a); (2) the minor intermediate may be responsible for the major diastereomeric product, because of greater reactivity (Fig. 1b).

While the latter behavior has been considered for generation of chirality in catalytic, homogeneous processes, in the diastereoselective Paternò–Büchi reaction the former is relevant, i.e., the major diastereoisomer arises from the preferentially formed intermediate, while the minor intermediate undergoes preferential retrocleavage.

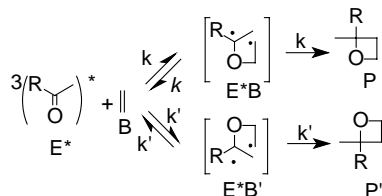
On the basis of the hypothesis of Sharf, we could conclude that in the Paternò–Büchi reaction the thermodynamic more stable product is formed.

In this paper we want to verify if regio- and stereochemistry of the Paternò–Büchi reaction on furan derivatives can be explained on the basis of the simple hypothesis that the most stable compound is formed. Furthermore, we want

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Scheme 1. The Scharf hypothesis on the stereoselectivity of the Paternò–Büchi reaction.

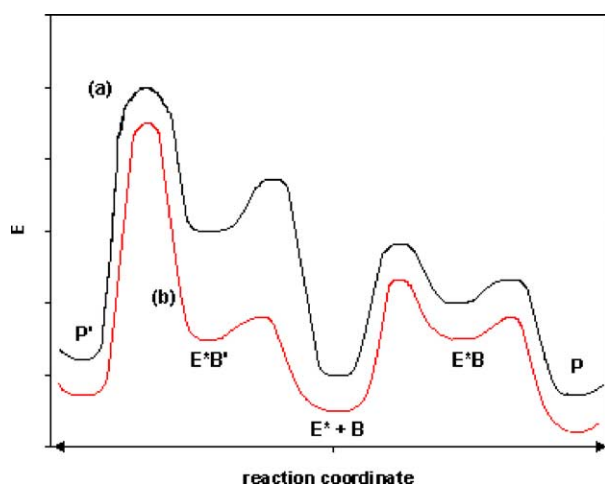


Fig. 1. Possible kinetic behaviors.

to verify if frontier orbitals interactions can play a role determining the regiochemistry of the reaction. Finally, we want to verify if the formation of most stable biradical intermediate can play a role in the stereochemical behavior of the reaction. We studied the photochemical coupling reaction of 2,3-dihydrofuran, furan, 2-methylfuran, and 2-furylmethanol with benzaldehyde. The aim of this work is to give a description able to discriminate between the possible products of the Paternò–Büchi reaction.

## 2. Materials and methods

NMR spectra were recorded on a Bruker 300 AM instrument or on a Varian Inova 500 instrument operating at 499.60. Elemental analyses were obtained using a Carlo Erba Elemental Analyzer 1106.

### 2.1. Caution

Performing the NMR spectra of cycloadducts we observed that deuterated chloroform purchased from Aldrich induced a retro-cycloaddition reaction giving, within an hour, the starting materials. We did not observe this behavior using deuterated chloroform from Fluka or Carlo Erba. We asked Aldrich about the presence of metals or some other trace impurities in deuterated chloroform which could give this

type of reaction. Until now, we have received a reply from Aldrich and we think we should advise readers on this possible problem.

#### 2.1.1. Reaction between benzaldehyde and 2-methylfuran

Benzaldehyde (0.38 g) was dissolved in furan (10 ml). The mixture was flushed with nitrogen for 20 min. The mixture was irradiated in an immersion apparatus with a 125 W high-pressure mercury arc (Helios-Italquartz) surrounded with a Pyrex water jacket for 24 h. The solvent was evaporated and the residue extracted with ether. The removal of the solvent yielded a crude product that was chromatographed on silica gel. The elution with toluene gave pure product. Yield: 86%.  $\delta_{\text{H}}$  (500 MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ) 7.5–7.2 (5 H, m), 6.53 (2 H, d,  $J = 4.5$  Hz), 5.57 (1 H, d,  $J = 3.5$  Hz), 5.11 (1 H, m), 3.66 (1 H, dd,  $J_1 = 4.5$  Hz,  $J_2 = 3.5$  Hz), and 2.03 (3 H, s);  $\delta_{\text{C}}$  ( $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ) 158.6, 141.6, 128.9, 128.3, 125.6, 108.7, 99.4, 93.1, 54.0, and 14.2 ppm (Found C, 76.01; H, 6.37.  $\text{C}_{12}\text{H}_{12}\text{O}_2$  requires C, 76.57; H, 6.43%).

## 3. Results and discussion

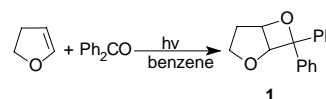
The irradiation of 2,3-dihydrofuran with benzophenone gave the adduct **1** (Scheme 2) [11].

The same behavior was observed irradiating 2,3-dihydrofuran with aliphatic aldehydes and ketones. By using acetone the adducts were obtained in a 200:1 isomeric ratio [12]. When benzaldehyde was used as carbonyl compounds the adducts were obtained as a >98:2 regioisomeric mixture. The major isomer is 88:12 *endo/exo* mixture. The reaction showed a good regio- and stereoselectivity [13–15].

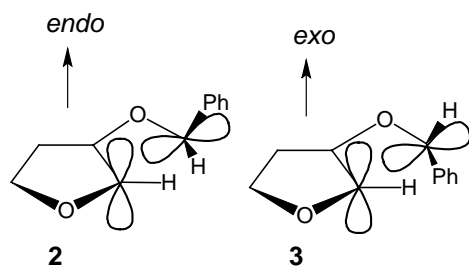
Benzaldehyde reacts in its triplet state. This way, a triplet biradical is formed as an intermediate. For the formation of the products, intersystem crossing into the singlet manifold is necessary. The most important factor influencing an intersystem crossing for flexible triplet biradicals is spin–orbit coupling. The angle between p orbitals at the radical centers is approximately  $90^\circ$  for maximum spin orbit coupling.

For the pronounced *endo* selectivity in the reaction between aromatic aldehydes and 2,3-dihydrofuran, we can consider the two biradical conformers **2** and **3** to be responsible, with the alkoxy substituent localized in a pseudoequatorial position and **2** being more populated because of fewer steric interactions (Scheme 3) [16,17].

We examined the regiochemistry of the reaction. On the basis of the theoretical work of Palmer et al. [8], we tested the possibility that the regiochemical behavior of the reaction is



Scheme 2. The Paternò–Büchi reaction on 2,3-dihydrofuran.



Scheme 3. Radical intermediate in the cycloaddition of benzaldehyde to 2,3-dihydrofuran.

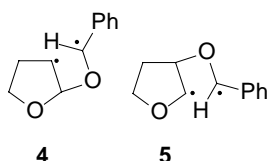


Fig. 2. Biradical intermediates in the reactions of 2,3-dihydrofuran with benzaldehyde.

determined by the formation of the more stable biradical intermediate. We performed some ab initio calculations using 6-31G\*\* basis set on Gaussian 98, using UHF method. The calculations were usually done using Møller–Plesset perturbations (MP2).

The Polak–Ribiere algorithm with gradient calculations was adopted for geometry optimizations. The open-shell states were treated at the same level of accuracy as the closed shell states. We verified that the obtained structures were minima on the potential energy surfaces calculating the frequencies of the optimized structures. We examined the structures **4** and **5** (Fig. 2).

Structure **4** is more stable than **5** for 2 kcal mol<sup>-1</sup>. This result is not in agreement with the experimental results.

An approach based on the frontier orbitals control is more efficient in order to explain the photochemical behavior. The HOMO of 2,3-dihydrofuran is at -0.32 eV and it is reported in Fig. 3. The atomic coefficients of the HOMO are in agreement with an attack of the LUMO (the carbonyl oxygen) on the  $\beta$  carbon.

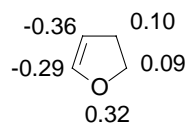


Fig. 3. Atomic coefficients of the HOMO of 2,3-dihydrofuran.

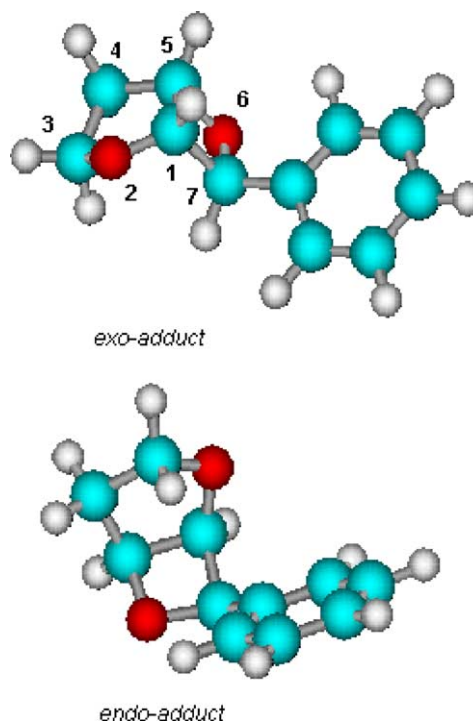


Fig. 4. Structures of the possible adducts between 2,3-dihydrofuran and benzaldehyde.

On the basis of this result we tested the thermodynamic stability of the possible adducts. The structures of these compounds are reported in Fig. 4 while some structural properties are collected in Table 1. We calculated the total electronic energy of these two molecules (Table 2).

We can see that the *endo* isomer is more stable for 2 kcal mol<sup>-1</sup> than the other isomer.

In conclusion, we have seen that the position of the formation of the first C–O bond is under frontier orbitals

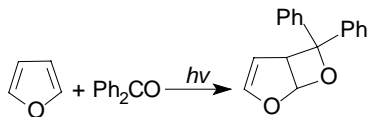
Table 1  
Structural properties of the possible adducts between 2,3-dihydrofuran and benzaldehyde

Adduct	Bond length (Å)							
	C <sub>1</sub> –O <sub>2</sub>	O <sub>2</sub> –C <sub>3</sub>	C <sub>3</sub> –C <sub>4</sub>	C <sub>4</sub> –C <sub>5</sub>	C <sub>5</sub> –C <sub>1</sub>	C <sub>5</sub> –O <sub>6</sub>	O <sub>6</sub> –C <sub>7</sub>	C <sub>7</sub> –C <sub>1</sub>
<i>exo</i>	1.392	1.412	1.532	1.519	1.534	1.422	1.426	1.546
<i>endo</i>	1.389	1.414	1.531	1.518	1.534	1.423	1.425	1.546
	Angle (°)							
	1–2–3	2–3–4	3–4–5	4–5–1	5–1–2	4–5–6	2–1–7	
<i>exo</i>	109.18	105.34	102.57	104.29	107.91	113.92	115.84	
<i>endo</i>	109.73	105.23	102.36	104.48	107.69	113.59	117.53	

Table 2

Total electronic energy of the possible adducts between 2,3-dihydrofuran and benzaldehyde

Adduct	Electronic state	Energy (kcal mol <sup>-1</sup> )
<i>exo</i>	S <sub>0</sub>	-360900
<i>endo</i>	S <sub>0</sub>	-360902



Scheme 4. Paternò-Büchi reaction between furan and benzophenone.

control. Furthermore, the best way to justify the formation of the *endo* isomer is to consider the formation of the most stable compound.

Schenk reported that the irradiation of benzophenone in furan gave the corresponding adduct in 94% yield (Scheme 4) [18,19].

Furan and 2-methylfuran were found to react with propanal and benzaldehyde [20]. The structure of the products was confirmed also by NOE analysis [21]. The *exo* configuration was assigned to the carbon at C-6 on the dioxabicyclo[3.2.0]heptene skeleton [22].

The Japanese group supposed that the reaction involved the formation of the biradical **6** (Fig. 5), due to the attack of the n,π\* triplet oxygen on the site of higher free valence or a more frontier electron density of the furan ring [20].

Afterwards, the same group tested the reaction on a large group of aliphatic and aromatic aldehydes and ketones [23]. They found that ketones reacted giving lower yields than the corresponding aldehydes: in particular acetone, butanone, and acetophenone gave yields in the range of 0.9–1.7%; furthermore, the oxetane yields increased with the number of carbon atoms: with acetaldehyde they obtained 15% yield, while cyclohexylcarbaldehyde gave 27% yield and benzaldehyde 35%.

The kinetics of the reaction is in agreement with a mechanism involving the formation of the biradical **6** [24].

The high *exo* stereoselectivity of the reaction has been extensively studied: the formation of the product occurs on a triplet 1,4-biradical which must be converted into the singlet biradical to give the product. As reported above, the reaction is determined by spin-orbit coupling (SOC). SOC is strongly dependent on the geometry of the triplet biradicals: in par-

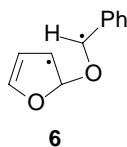
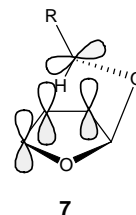
Fig. 5. The biradical intermediate **6**.**7**

Fig. 6. Possible biradical intermediate in the reaction between furan and an aldehyde.

ticular, SOC decreases with increasing distance between the two spin-bearing atoms. The best geometry to have SOC requires that the axes of the p orbitals at the radical centers are perpendicular to each other. In order to explain the pronounced *exo* stereoselectivity, a secondary orbital effect can be postulated: an interaction between the rather flexible α-oxy radical center and the allyloxy ring localized radical in **7**, likely plays a major role (Fig. 6) [16,25].

On the basis of the above reported results we examined the Paternò-Büchi reaction on furan. The HOMO of furan has energy of -0.32 eV and the atomic coefficients of this orbital (Fig. 7) are in agreement with an attack of the carbonyl oxygen on the α carbon.

The structures of the possible adducts deriving from the attack of benzaldehyde in the α position of furan are depicted in Fig. 8. Some structural properties of these structures are reported in Table 3.

We calculated the total electronic energy of these two structures (Table 4).

We can see that the *exo* isomer is more stable (0.5 kcal mol<sup>-1</sup>) than the other isomer.

Two years later the first report on the reactivity of furan 2-methylfuran was found to react with propanal and benzaldehyde [20]. A mixture of regioisomeric products was obtained, but the authors did not report the regioisomeric ratio. In contrast with this result, other authors reported a complete regioselectivity in the reaction between substituted furans and benzophenone: in these reactions the coupling occurred on the most hindered side of the molecule (Scheme 5) [26,27].

On the contrary, a completely different regioselectivity was described in a synthesis of oxetanocin. Oxetanocin was obtained carrying out the reaction between 2-methylfuran and benzoyloxyacetaldehyde. The corresponding adduct was treated with ozone and the product was reduced with NaBH<sub>4</sub>. The obtained alcohols were protected. Product **8** was treated with *N*-benzoyl-disilyladenine and SnCl<sub>4</sub> to give **9** (Scheme 6) [28].

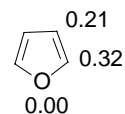


Fig. 7. Atomic coefficients of the HOMO of furan.

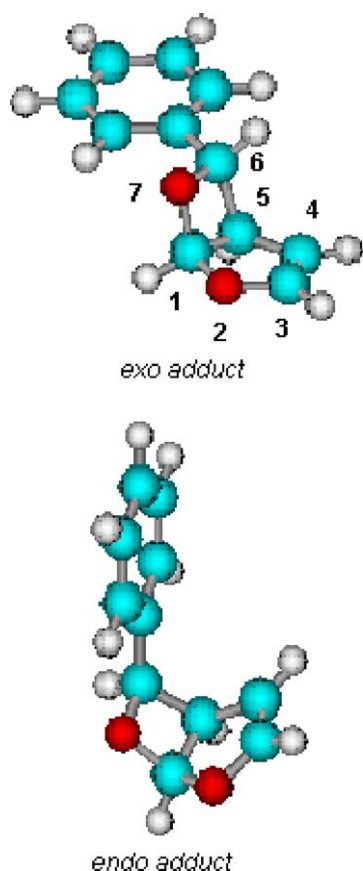


Fig. 8. Structures of the possible adducts between furan and benzaldehyde.

Furthermore, in the reaction of 2-methylfuran with a phenylglyoxylate derivative, a mixture of regioisomers was obtained (Scheme 7) [29].

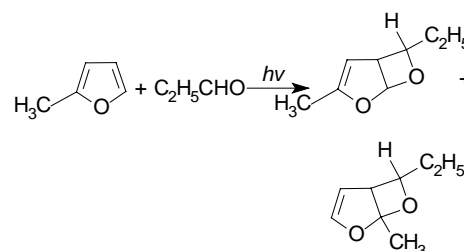
On the basis of the above-reported data, we are not able to predict the regioselectivity in the reaction of 2-methylfuran with carbonyl compound. In order to have a sure reference datum for our calculation we performed the reaction between 2-methylfuran and benzaldehyde (Scheme 8). We obtained only the regioisomers **10** deriving from the attack on the less hindered side of the molecule.

We examined the Paternò–Büchi reaction on 2-methylfuran. The HOMO of 2-methylfuran showed the atomic

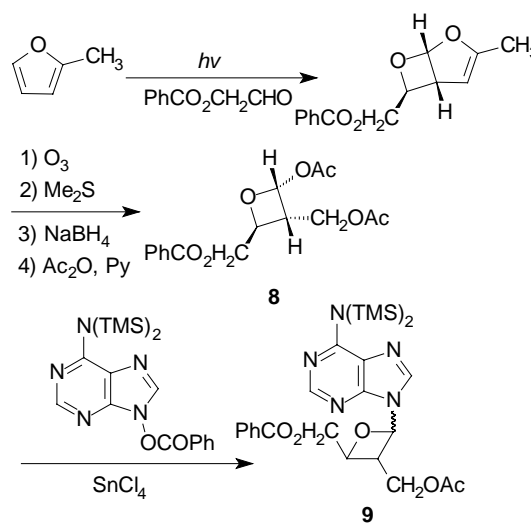
Table 4

Total electronic energy of the possible adducts between furan and benzaldehyde

Adduct	Electronic state	Energy (kcal mol <sup>-1</sup> )
exo	S <sub>0</sub>	-358972.09
endo	S <sub>0</sub>	-358971.60



Scheme 5. Paternò–Büchi reaction between 2-methylfuran and a carbonyl compound.

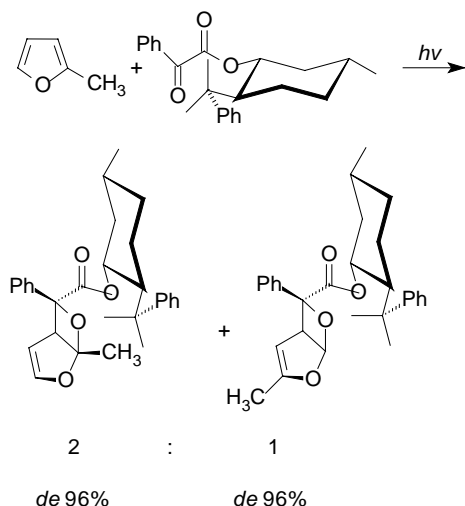


Scheme 6. Paternò–Büchi reaction on 2-methylfuran in the synthesis of oxetanocin.

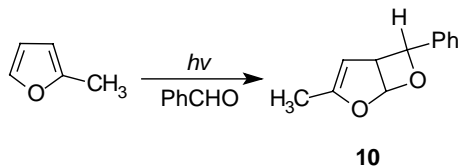
Table 3

Structural properties of the possible adducts between furan and benzaldehyde

Adduct	Bond length (Å)							
	C <sub>1</sub> –O <sub>2</sub>	O <sub>2</sub> –C <sub>3</sub>	C <sub>3</sub> –C <sub>4</sub>	C <sub>4</sub> –C <sub>5</sub>	C <sub>5</sub> –C <sub>1</sub>	C <sub>5</sub> –C <sub>6</sub>	C <sub>6</sub> –O <sub>7</sub>	O <sub>7</sub> –C <sub>1</sub>
exo	1.397	1.359	1.318	1.505	1.536	1.551	1.428	1.398
endo	1.395	1.361	1.316	1.504	1.535	1.551	1.427	1.399
Adduct	Angle (°)							
	1–2–3	2–3–4	3–4–5	4–5–1	5–1–2	4–5–6	2–1–7	
exo	107.32	115.18	108.24	100.78	108.05	115.89	113.83	
endo	107.02	115.19	108.34	100.55	108.29	116.93	113.68	



Scheme 7. Paternò-Büchi reaction between 2-methylfuran and a phenylglyoxylate derivative.



Scheme 8. Paternò-Büchi reaction between 2-methylfuran and benzaldehyde.

coefficients reported in Fig. 9. These data are in agreement with an attack of the carbonyl oxygen on the  $\alpha$  carbon.

The structures of the possible adducts deriving from the attack of benzaldehyde in the  $\alpha$  position of 2-methylfuran are depicted in Figs. 10 and 11. Some structural properties of these structures are reported in Table 5.

We calculated the total electronic energy of these four structures (Table 6).

The formation of the *exo* isomers of both 1,2 and 4,5 adducts is favored. Furthermore, the 4,5-adduct is favored for  $0.86 \text{ kcal mol}^{-1}$ . This energy difference allows to explain the observed regioselectivity. Furthermore, we considered the energy of the possible biradical intermediates **11** and **12** (Fig. 12).

The biradical intermediate **12** is favored for  $1.18 \text{ kcal mol}^{-1}$ , in agreement with the observed regioselectivity.

2-Furylmethanol and the corresponding silyl ether gave low regioselectivity (Scheme 9) [30–32].

The HOMO of 2-furylmethanol showed the atomic coefficients reported in Fig. 13. These data are in agree-

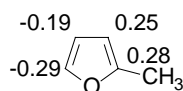


Fig. 9. Atomic coefficients of the HOMO of 2-methylfuran.

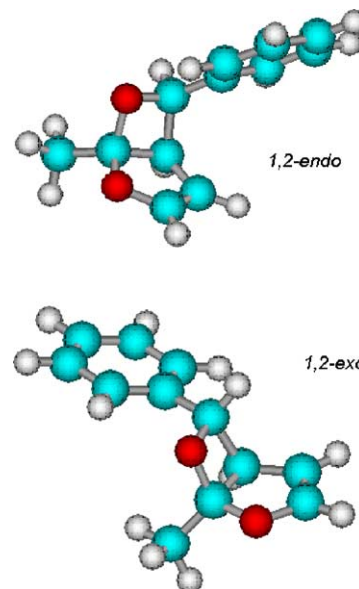


Fig. 10. Structures of the possible adducts between 2-methylfuran and benzaldehyde deriving from the attack on the most hindered side of the molecule.

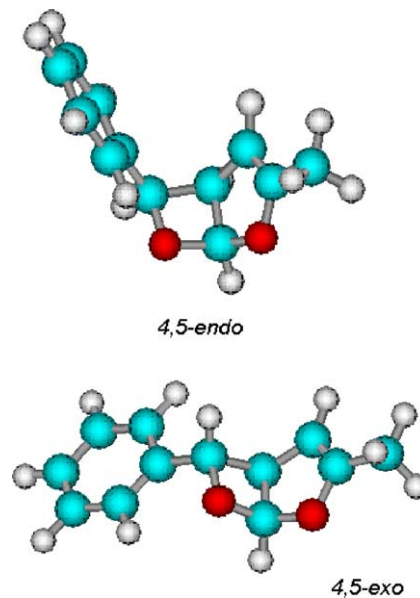


Fig. 11. Structures of the possible adducts between 2-methylfuran and benzaldehyde deriving from the attack on the less hindered side of the molecule.

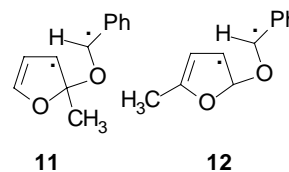


Fig. 12. Biradical intermediates in the reactions of 2-methylfuran with benzaldehyde.

Table 5  
Structural properties of the possible adducts between 2-methylfuran and benzaldehyde

Adduct	Bond length (Å)							
	C <sub>1</sub> –O <sub>2</sub>	O <sub>2</sub> –C <sub>3</sub>	C <sub>3</sub> –C <sub>4</sub>	C <sub>4</sub> –C <sub>5</sub>	C <sub>5</sub> –C <sub>1</sub>	C <sub>5</sub> –C <sub>6</sub>	C <sub>6</sub> –O <sub>7</sub>	O <sub>7</sub> –C <sub>1</sub>
1,2- <i>exo</i>	1.407	1.356	1.318	1.504	1.543	1.547	1.427	1.406
1,2- <i>endo</i>	1.403	1.359	1.317	1.503	1.542	1.549	1.425	1.407
4,5- <i>exo</i>	1.395	1.366	1.321	1.503	1.535	1.549	1.428	1.400
4,5- <i>endo</i>	1.393	1.367	1.320	1.502	1.535	1.552	1.427	1.401
	Angle (°)							
	1–2–3	2–3–4	3–4–5	4–5–1	5–1–2	4–5–6	2–1–7	
1,2- <i>exo</i>	107.87	115.33	108.08	101.42	107.10	115.55	112.00	
1,2- <i>endo</i>	107.55	115.29	108.23	101.11	107.44	116.78	112.06	
4,5- <i>exo</i>	107.92	113.94	109.02	100.61	108.00	115.76	113.66	
4,5- <i>endo</i>	107.72	113.97	109.06	100.49	108.17	117.03	113.69	

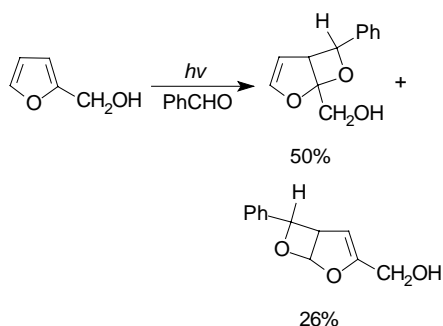
Table 6  
Total electronic energy of the possible adducts between 2-methylfuran and benzaldehyde

Adduct	Electronic state	Energy (kcal mol <sup>-1</sup> )
1,2- <i>exo</i>	S <sub>0</sub>	-383474.83
1,2- <i>endo</i>	S <sub>0</sub>	-383474.54
4,5- <i>exo</i>	S <sub>0</sub>	-383475.69
4,5- <i>endo</i>	S <sub>0</sub>	-383475.27

ment with an attack of the carbonyl oxygen on the  $\alpha$  carbon.

The structures of the possible adducts deriving from the attack of benzaldehyde in the  $\alpha$  position of 2-furylmethanol are depicted in Figs. 14 and 15. Some structural properties of these structures are reported in Table 7.

We calculated the total electronic energy of these four structures (Table 8).



Scheme 9. Paternò–Büchi reaction between 2-furylmethanol and benzaldehyde.

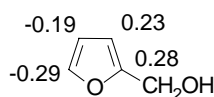


Fig. 13. Atomic coefficients of the HOMO of 2-furylmethanol.

The data in Table 8 showed that the *exo* stereoisomer is favored for all the regioisomers. On the basis of these data the attack on the most hindered side of the molecule should be favored for 2 kcal mol<sup>-1</sup>. However, considering the results obtained studying the reactivity of 2-methylfuran, we considered the relative stability of the possible biradical intermediates **13** and **14** (Fig. 16).

The calculations of these biradicals showed that **13** is more stable than **14** for 0.8 kcal mol<sup>-1</sup>. This difference could account for the preferential formation of the product deriving

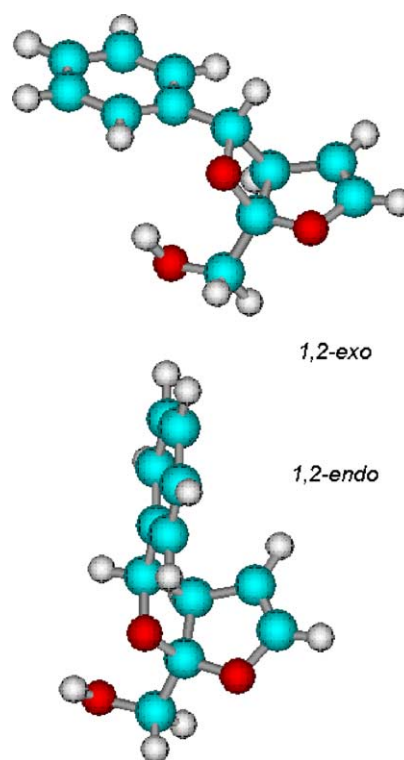


Fig. 14. Structures of the possible adducts between 2-furylmethanol and benzaldehyde deriving from the attack on the most hindered side of the molecule.

Table 7  
Structural properties of the possible adducts between 2-furylmethanol and benzaldehyde

Adduct	Bond length (Å)							
	C <sub>1</sub> –O <sub>2</sub>	O <sub>2</sub> –C <sub>3</sub>	C <sub>3</sub> –C <sub>4</sub>	C <sub>4</sub> –C <sub>5</sub>	C <sub>5</sub> –C <sub>1</sub>	C <sub>5</sub> –C <sub>6</sub>	C <sub>6</sub> –O <sub>7</sub>	O <sub>7</sub> –C <sub>1</sub>
1,2- <i>exo</i>	1.404	1.360	1.317	1.504	1.539	1.548	1.431	1.404
1,2- <i>endo</i>	1.399	1.363	1.316	1.503	1.538	1.550	1.431	1.407
4,5- <i>exo</i>	1.400	1.367	1.319	1.503	1.535	1.553	1.430	1.395
4,5- <i>endo</i>	1.396	1.369	1.318	1.504	1.534	1.550	1.429	1.399
	Angle (°)							
	1–2–3	2–3–4	3–4–5	4–5–1	5–1–2	4–5–6	2–1–7	
1,2- <i>exo</i>	107.84	115.22	108.09	101.48	107.35	115.95	112.99	
1,2- <i>endo</i>	107.54	115.11	108.28	101.07	107.78	117.27	113.13	
4,5- <i>exo</i>	107.94	114.25	108.79	101.05	107.68	115.82	113.91	
4,5- <i>endo</i>	107.50	114.22	108.92	100.56	108.08	116.85	113.78	

from the attack on the most hindered side of the molecule. Furthermore, it can account for the formation of two regioisomers.

In conclusion, we have shown that the regiochemical behavior (the attack of the oxygen on an  $\alpha$  carbon or on a  $\beta$  carbon of the furan ring) of the Paternò–Büchi reaction on 2,3-dihydrofuran, furan, 2-methylfuran, and 2-furylmethanol can be explained considering the atomic coefficients of the HOMOs. Furthermore, the stereochemical behavior can be explained, on the basis of the Scharf's hypothesis, considering the formation of the most stable stereoisomer. The origin of this behavior can be found in the spin control formulated by Greisbeck. Finally, the

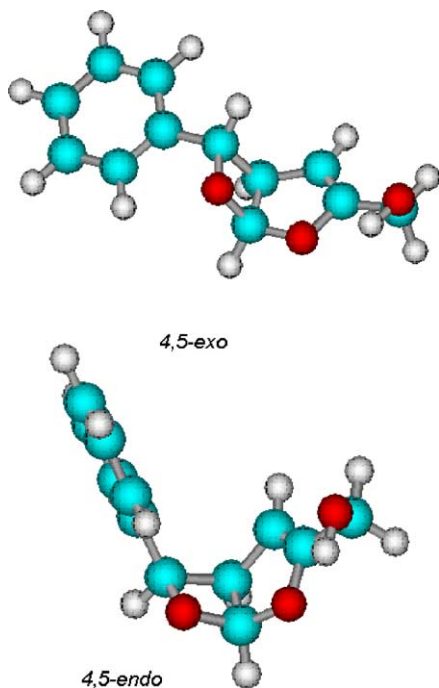


Fig. 15. Structures of the possible adducts between 2-furylmethanol and benzaldehyde deriving from the attack on the less hindered side of the molecule.

Table 8  
Total electronic energy of the possible adducts between 2-furylmethanol and benzaldehyde

Adduct	Electronic state	Energy (kcal mol <sup>-1</sup> )
1,2- <i>exo</i>	S <sub>0</sub>	-430446.65
1,2- <i>endo</i>	S <sub>0</sub>	-430446.03
4,5- <i>exo</i>	S <sub>0</sub>	-430444.27
4,5- <i>endo</i>	S <sub>0</sub>	-430443.84

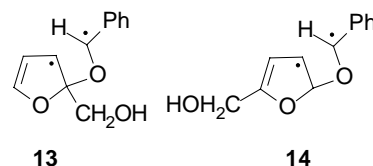


Fig. 16. Biradical intermediates in the reactions of 2,3-dihydrofuran with benzaldehyde.

regiochemical behavior on monosubstituted furan can be explained on the basis of both the relative stability of the possible biradical intermediates, where the most stable one is favored, and the relative stability of the possible adducts: both the approach can explain the observed regiochemistry.

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