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STUDY OF THE DIELS-ALDER AND RETRO-DIELS-ALDER REACTION BETWEEN FURAN DERIVATIVES AND MALEIMIDE FOR THE CREATION OF NEW MATERIALS

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Abstract

The Diels-Alder reaction leads to a mixture of two diastereomers, one called endo and the other one exo. The cyclo-reversion temperature of the first one is lower than the exo adduct and the ratio between endo and exo adduct varies according to substituents of Diels-Alder partners and experimental parameters. Therefore, the influence of some reaction parameters such as the substituents of furan and maleimide derivatives, the reaction temperature and the presence of a nucleophile on the endo/exo Diels-Alder ratio and/or the retroDiels-Alder reaction have been studied. For instance, furan and maleimide derivatives with electro withdrawing substituents induced the creation of the endo adduct preferentially. Also the presence of far electron withdrawing substituent on furan and/or an electron attracting mesomeric on maleimide implied a faster reversibility of the endo adduct. Finally, a high temperature and the presence of a nucleophile (thiol) also induced a faster retroDiels-alder kinetic. Moreover, it was proved that isomerization from endo to exo diastereomer is preceded by a retroDiels-Alder of the endo adduct. The presence of a nucleophile in the mixture confirmed this result.
This study allowed highlighting different parameters of Diels-Alder reaction to obtain more endo adduct as possible, a fast and/or full retroDiels-Alder of this one.

Keywords

retroDiels-Alder kinetic, Michael addition, Fast unprotection, Maleimide derivatives, Furan derivatives

Highlight

-The more the substituent of furan and maleimide derivatives are electron withdrawing, the more the endo adduct is obtained;

-The NMR analysis is the best method to determine a retroDiels-Alder temperature;

-When the substituent of the furan derivative is far electron withdrawing the retroDiels-Alder of endo adduct is fast;

-When the substituent of the maleimide derivative is electron attracting mesomeric the retroDiels-Alder of endo adduct is fast;

-Prior to endo to exo diasteromer isomerization, the retroDiels-Alder reaction of the endo adduct occurred;

-The presence of a nucleophile proves the isomerization hypothesis and allows a faster unprotection of Diels-Alder adducts.

1 Introduction

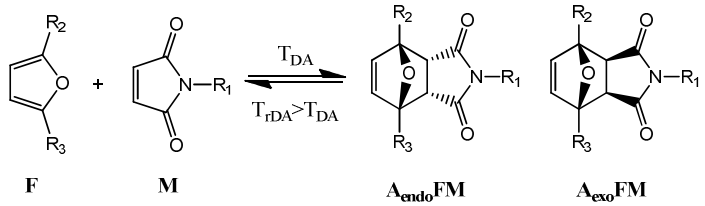
« Self-healing » materials[1-3] and materials which present a post-crosslinking on demand represent a huge interest for scientists. In both cases, stimuli reversible reactions and controlled reactions (or bonds) are used. Temperature, radiation, O_2, UV, Electron beam, X-ray, water, pH etc. are commonly used as external stimuli. For this study, the temperature, which is the easier way for industrialization, has been chosen. Systems as urethane group[4], nitroso group[5], ester group[6], ionene complex[7-10], azlactone-phenol adduct[11, 12] and, lastly, the Diels-Alder adduct[13-18] allow the formation of reversible covalent bonds under high temperature conditions. Diels-Alder system was chosen for this project, in spite of existing studies[14, 19-21], because this is the most famous and the easier system. The Diels-Alder reaction already proved its significance for the formation of reversible covalent bonds formation[22, 23] or for the synthesis of new polymers/materials having intermittent life. Among them, thermo-sensitive surfactants[24], self-healing materials[25], high and mild temperature reversible materials[26]and materials having a controlled crosslinking reaction[27] can be found. This study on Diels-Alder reaction will help to improve the control of crosslinking reaction during materials formation.

Indeed, the Diels-Alder cycloaddition reaction would benefit from being upgraded on blocking and unblocking temperature, particularly by studying the influence of reactant substituents on the Diels-Alder and retroDiels-alder reaction, to upgrade adduct stereochemistry and the kinetic of the reaction, respectively. The selectivity of the Diels-Alder reaction between maleimide and maleic anhydride[28] has already been studied. Also, some study has been done on the influence of both furan and maleimides derivatives. However, those results were used to study the endergonic and exergonic behavior of the Diels-Alder reaction[29]. Moreover, those results were obtained by computerized simulation, and only few examples have been experimentally studied. It is also important to notice that the reaction between furan and maleimide are often concerted cycloaddition, but due to nucleophilic character of furan derivatives, the reaction with p-electron deficient components, as maleimide, may proceed via asynchronous transition state and in extremely case, a stepwise zwitterionic mechanism is also possible[30, 31].

It is interesting to go further on structure of products used for the Diels-alder reaction and on the characterisation of the cyclo-reversion reaction. The main goal of this publication is to establish the precise rules of furan and maleimides derivatives substituents on Diels-Alder and retroDiels-Alder reactions.

2 Results and discussion

It is well known that the Diels-Alder (DA) reaction leads to a mixture of two diastereomers compounds, one call endo (the kinetic compound) and the other exo (the thermodynamic compound)[13, 32] (Scheme 1). For simplicity the adduct formed after the DA is called as followed: **A** for Adduct, then endo or exo depending on the adduct obtained (if there is nothing after **A**, it means that it is a mixture), then **F** and **M** for the Furan and the Maleimide derivatives, respectively.

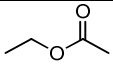
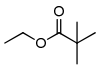
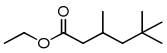
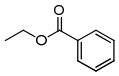
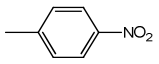
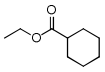
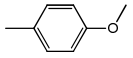
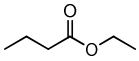
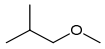
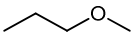
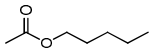
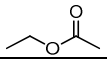


Scheme 1: Diastereomers obtained after Diels-Alder reaction between furan (F) and maleimide (M)

During the reverse reaction, called retroDiels-Alder (rDA), the endo compound is first unblocked[33], i.e. at lower temperature than the exo compound. As a consequence, the parameters affecting the diastereoselectivity (structure, experimental conditions, solvent, temperatures, etc…) have to be controlled to upgrade the obtaining of endo adduct, giving thus the possibility to break it at average temperature and give the maleimide double bond's reactivity back. Some studies deal with the Diels-Alder between furan and maleimide derivatives but there is a lack of precision about the control of all these parameters. First, a complete modeling study has been carried out to get all the information to control them. For that, the maleimide/furan derivatives system[1, 13, 14, 34] is studied thanks to existing compound (commercial, ***c***) or synthetized compound (***s***) (Table 1).

All products were chosen to have the widest diversity of partners for the DA reaction, with various characteristics (electronic and hindering effect). It is established that the DA reaction is a spontaneous reaction between a diene, i.e. furan derivatives, and a dienophile, i.e. maleimide derivatives. Furan derivatives are described, in the literature, as very good dienes for the DA reaction. Indeed, the oxygen atom enables the relocation of diene double bonds and increases the reactivity of these doublets. For maleimide derivatives, electrons attracting mesomeric substituents (imides) on both sides of the double bond allow increasing the reactivity regarding dienes. In this way, furan derivatives and maleimides react quickly together at room temperature (20°C). They are also known to give low retroDiels-Alder temperature (~110°C)[35].

Table 1: Structures of different commercial (c) or synthesized (s) furan (F) and maleimide (M) derivatives

R_2	R_3	Blocking agent	Mass yield (%)	R_1	Maleimide	Mass yield (%)
	H	**F_1** ***(c)***	/		**M_1** ***(c)***	/
	H	**F_2** ***(s)***	95		**M_2** ***(s)***	57
	H	**F_3** ***(s)***	87		**M_3** ***(s)***	56
	H	**F_4** ***(s)***	99		**M_4** ***(s)***	62
	H	**F_5** ***(s)***	86		**M_5** ***(s)***	64
	H	**F_6** ***(c)***	/		**M_6** ***(s)***	74
	H	**F_7** ***(c)***	/		**M_7** ***(s)***	72
	H	**F_8** ***(s)***	95			
		**F_9** ***(s)***	88			

It is worth to note that the presence of substituents on those partners can facilitate the reaction (attracting inductive substituent on the diene and electron attracting mesomeric substituent on dienophile[36-41]) or destabilize the final adduct (hindering substituent). Indeed, it's known that the addition of substituent on both partners can have a real influence on the ratio between the endo and the exo compounds, but also on the stability of the adduct obtained after Diels-Alder. That is why some R_1 substituents on maleimide, R_2/R_3 on furan derivatives are added. These substituents could be electro donating, electro withdrawing, electron attracting and donating mesomeric or hindering substituent. Thus, Diels-Alder compounds can be formed with some pairs of **F** and **M**. The results are separated in two groups, the first one with various furan derivatives (Table 2) and the second one with various of maleimide (Table 3).

Table 2: Results on endo/exo ratio adduct of Diels-Alder reaction between N-methylmaleimide (M_1) or N-dodecylmaleimide (M_2) and furan derivatives (F)

Adduct	F	M	R (%)	T (°C)	Solvent	endo (%)*	exo (%)*
$\mathbf{AF_1M_1}$	$\mathbf{F_1}$	$\mathbf{M_1}$	94	23	DCM	77	23
$\mathbf{AF_2M_1}$	$\mathbf{F_2}$	$\mathbf{M_1}$	92	23	DCM	71	29
$\mathbf{AF_3M_1}$	$\mathbf{F_3}$	$\mathbf{M_1}$	96	23	DCM	73	27
$\mathbf{AF_4M_1}$	$\mathbf{F_4}$	$\mathbf{M_1}$	90	23	DCM	70	30
$\mathbf{AF_5M_1}$	$\mathbf{F_5}$	$\mathbf{M_1}$	95	23	DCM	71	28
$\mathbf{AF_6M_1}$	$\mathbf{F_6}$	$\mathbf{M_1}$	95	23	DCM	61	39
$\mathbf{AF_7M_1}$	$\mathbf{F_7}$	$\mathbf{M_1}$	98	23	DCM	87	13
$\mathbf{AF_9M_1}$	$\mathbf{F_9}$	$\mathbf{M_1}$	99	23	DCM	73	27
$\mathbf{AF_1M_2}$	$\mathbf{F_1}$	$\mathbf{M_2}$	85	23	THF	64	36
$\mathbf{AF_2M_2}$	$\mathbf{F_2}$	$\mathbf{M_2}$	83	23	THF	62	38
$\mathbf{AF_3M_2}$	$\mathbf{F_3}$	$\mathbf{M_2}$	87	23	THF	62	38
$\mathbf{AF_4M_2}$	$\mathbf{F_4}$	$\mathbf{M_2}$	92	23	THF	63	37
$\mathbf{AF_5M_2}$	$\mathbf{F_5}$	$\mathbf{M_2}$	88	23	THF	64	36
$\mathbf{AF_6M_2}$	$\mathbf{F_6}$	$\mathbf{M_2}$	93	23	THF	60	40

*Determined by ^{1}H NMR

After an ^{1}H NMR analysis of all Diels-Alder adducts, for example the $\mathbf{AF_1M_1}$ adduct (Figure 2), the ratio endo/exo is determined for each one. To calculate these ratios, the peaks corresponding to endo or exo adduct are used. To determine them, the system is analyzed with the Karplus equation (Equation 1) on vicinal protons H_c and H_d. The Karplus rule links the angle between the germinal protons and their constant coupling[42]. Thus, the theoretical coupling constant of protons H_c should be higher for the endo diastereomer. The comparison between theoretical ($^3J_{HcHd}$ = 5.5Hz) and experimental ($^3J_{HcHd}$ = 5.8Hz) constant coupling value for $\mathbf{A_{endo}F_1M_1}$ enabled attributing peaks for the endo and exo H_c proton (Figure 1, Figure 2). The angle between the two germinal protons of $\mathbf{A_{exo}F_1M_1}$ adduct (83.8°), was to close from the Karplus limit to afford accurate results. Nevertheless, the value obtained, from the Karplus equation, for the exo adduct indicated that the coupling constant should be lower compare to the endo adduct and near to a 0 Hz coupling constant. Thus, the experimental value of 1,6Hz confirmed the theoretical one (Figure 1, Figure 2). Therefore, the integration of c and c1 peaks, allowed attributing all other peaks by integration comparison (called x for the endo adduct and x1 for the exo adduct). Moreover, the endo/exo ratio is determined thanks to c and c1 integrations, which give the percentage of exo or endo adduct.

$^3J = 8.5 \cos2\ \Theta - 0.28$ for $0° < \Theta < 90°$
and $^3J = 9.5 \cos2\ \Theta - 0.28$ for $90° < \Theta < 180°$

Equation 1: Karplus equation

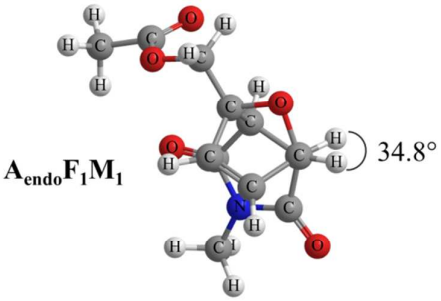


Figure 1: Molecular representation of $A_{endo}F_1M_1$, determination of the angle between H_c and H_d protons and experimental and theoretical coupling constant determination $^3J_{HcHd}$

Table 3: Results on endo/exo ratio adducts (AF_1M_x) of Diels-Alder reaction between furfuryl acetate (F_1) and maleimide derivatives (M)

Adduct	F	M	R (%)	T (°C)	Solvent	endo (%)*	exo (%)*
AF_1M_1	F_1	M_1	96	23	DCM	77	23
$A_{endo}F_1M_1$			94	23	Ether	100	0
AF_1M_2	F_1	M_2	92	23	THF	64	36
AF_1M_3	F_1	M_3	90	23	DCM	65	35
AF_1M_4	F_1	M_4	89	23	DCM	55	45
AF_1M_5	F_1	M_5	91	23	DCM	67	33
AF_1M_6	F_1	M_6	93	23	DCM	76	24
AF_1M_7	F_1	M_7	88	23	DCM	75	25

*Determined by ^{1}H NMR

The Diels-Alder reaction occurs efficiently between all furan and maleimide derivatives. Moreover, the ratio is always higher for the endo adduct which is the kinetic product, but when the temperature is increased the ratio of the exo adduct is increased at the same time. The ratio could be increased for the endo adduct if the substituent is electron withdrawing for the furan and/or the maleimide derivative. The increase of the ratio in favor of one of the diastereomer compare to the other is well known but the interest of this work is principally axed on the rDA of each adduct and the effect of some parameters on it.

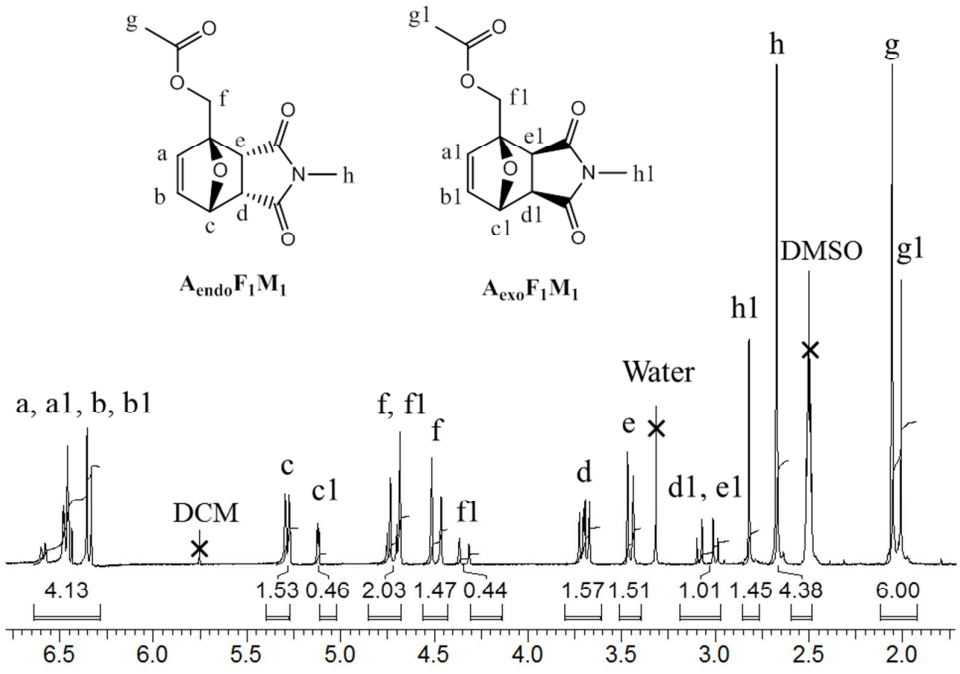


Figure 2: ^{1}H NMR spectrum of the AF_1M_1 adduct

2.1 Characterization of the retroDiels-Alder reaction

According to literature, the endo compound[33] is unblocked at a lower temperature than the exo compound. IR[43, 44], ^{1}H NMR[45, 46] and DSC[33, 47] analysis are generally used for the study of maleimide unblocking (retroDiels-Alder) reaction. The DSC was performed on the **AF_1M_1** adduct and the spectrum (Figure 3) and showed an endothermic peak starting at 80°C with a decrease until 110°C (region **I**, **rDA endo**) corresponding to the endo's unblocking reaction. Then an other endothermic peak begins at 110°C until a maximum point at 130°C (region **II**, **rDA exo**) corresponding to the exo's unblocking reaction[33].

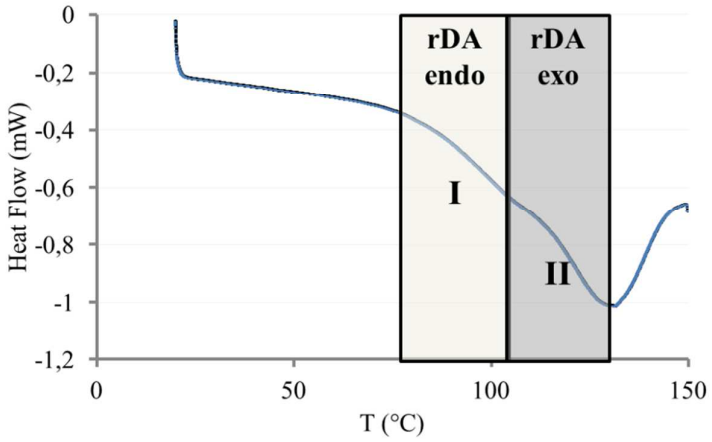


Figure 3: DSC Analysis of N-methylmaleimide (M_1)/ furfuryl acetate (F_1) Diels-Alder adduct

The DSC analysis was also performed on the adduct $\mathbf{A_{endo}F_1M_1}$ and the analysis showed one endothermic peak with a maximum point at 120°C corresponding to the unblocking reaction of the compound $\mathbf{A_{endo}F_1M_1}$. Then an isothermal analysis, of the same compound, at 70°C during 4 hours in DSC was performed and no endothermic peak was observed, proving that no unblocking reaction occurred.

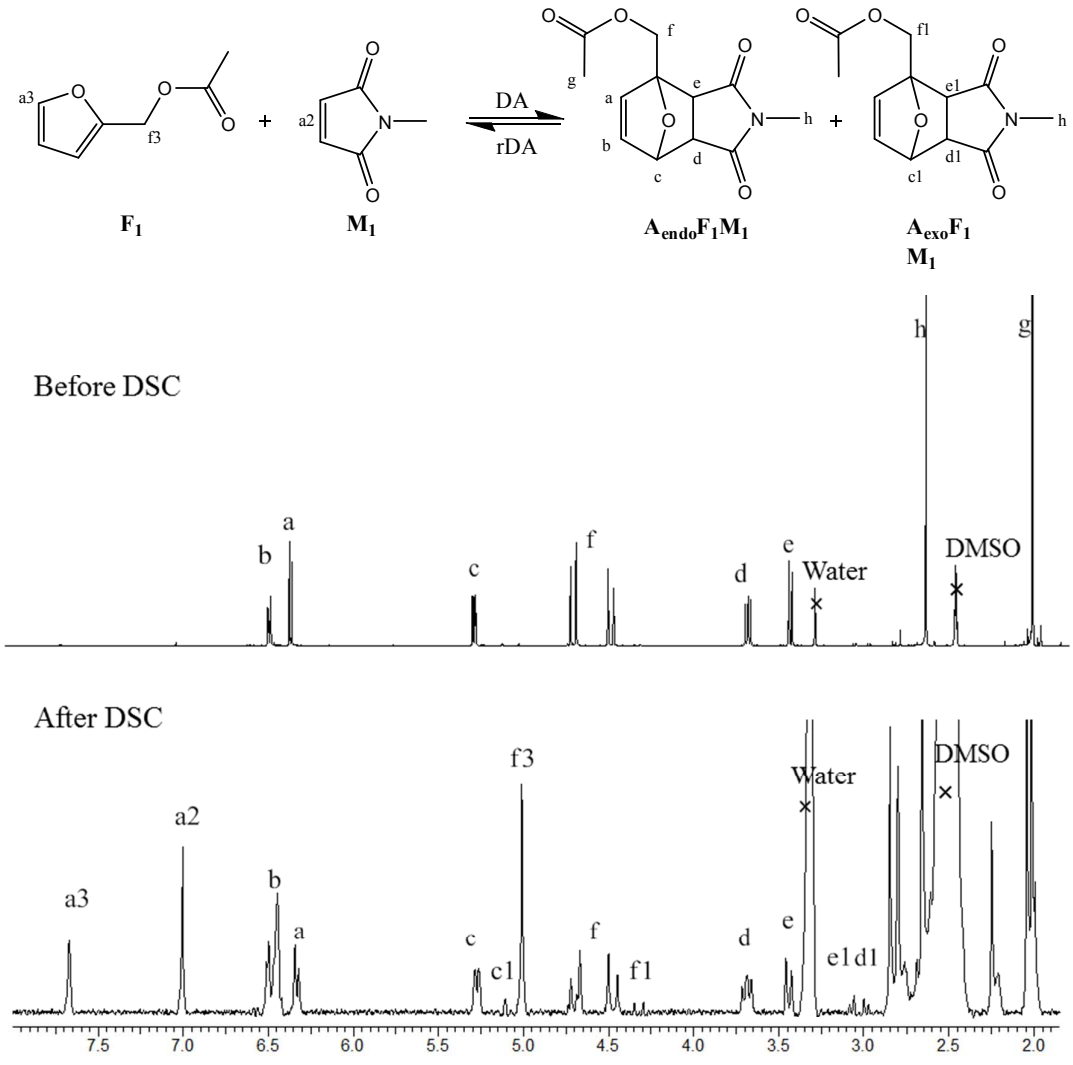


Figure 4: ^{1}H NMR Analysis of the capsule content after an isothermal DSC of the $\mathbf{A_{endo}F_1M_1}$ adduct during 4 hours in DMSO at 70°C

After this isothermal experiment in DSC, a ^{1}H NMR of the capsule content was done and the characteristic peaks of furan $\mathbf{F_1}$ and maleimide $\mathbf{M_1}$ appeared on the spectra, implying that a retroDiels-Alder of $\mathbf{A_{endo}F_1M_1}$ occurred (Figure 4). Moreover, the peaks of adduct $\mathbf{A_{exo}F_1M_1}$ appeared at 5.1 (c1), 4.35 (f1) and 3 ppm (e1 and c1), confirming an isomerization of the endo adduct. Thus, the ^{1}H NMR showed that the starting material ($\mathbf{A_{endo}F_1M_1}$) has been unblocked and the free maleimide $\mathbf{M_1}$ undergoes through a DA reaction with $\mathbf{F_1}$ to give $\mathbf{A_{exo}F_1M_1}$ adduct.

In the literature, the Diels-Alder temperature is generally determined by DSC analysis and the retroDiels-Alder temperature corresponds to the endothermic[47] peak's maximum. However, the retroDiels-Alder of the endo adduct is actually lower. Thanks to the last experiment, DSC analysis is not an appropriate analytical tool to precisely detect Diels-Alder or retroDiels-Alder reactions temperature. In this study the ^{1}H NMR is used as analytical tool to obtain precise results on endo and exo compounds, on Diels-Alder ratio and on retroDiels-Alder temperatures.

A model study of the Diels-Alder and retroDiels-Alder reaction for all adduct of table 4. As an example the reaction between of N-dodecylmaleimide (**M_2**) and cyclohexancarboxylate furfuryl (**F_5**) has been carried out in thermal ^{1}H NMR (Figure 5).

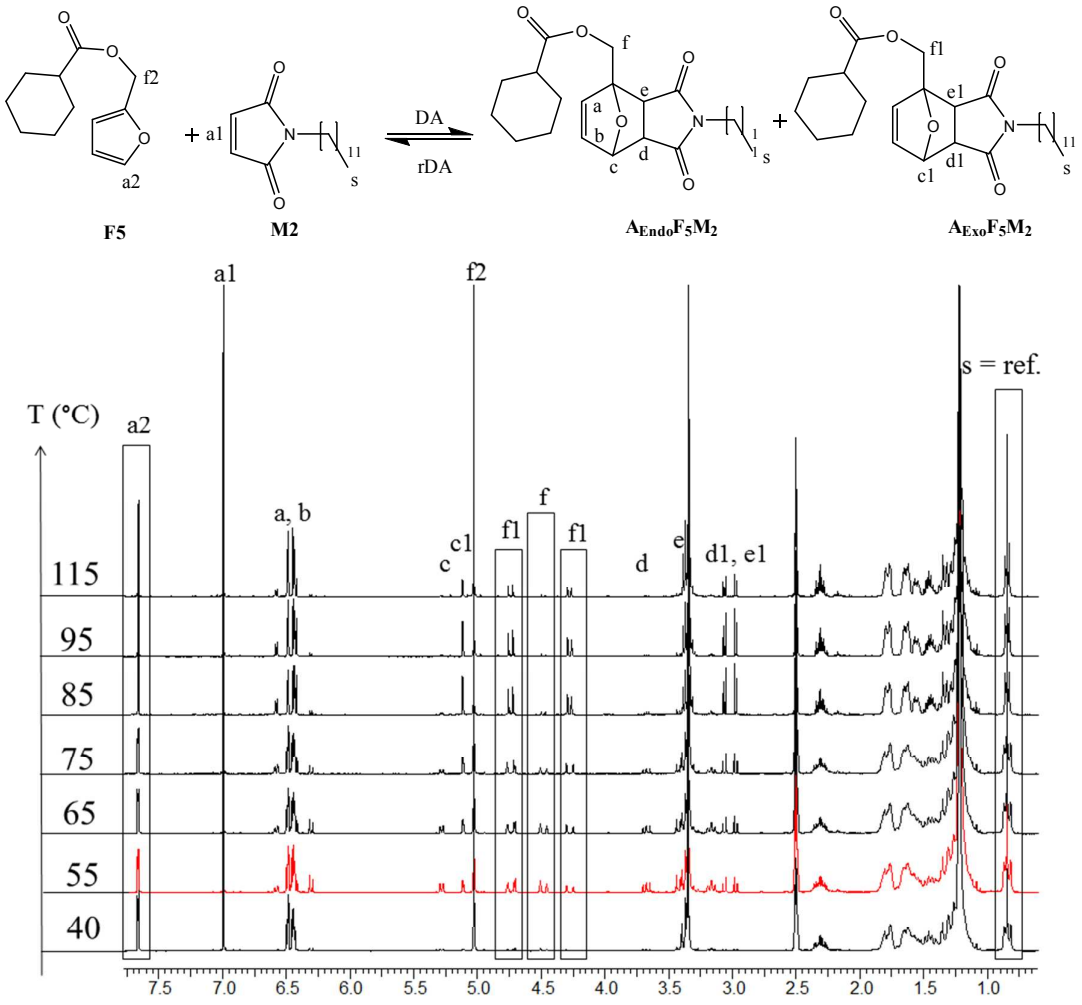


Figure 5: Temperature ^{1}H NMR spectrum overlaying of the Diels-Alder and retroDiels-Alder reaction of adducts AF_5M_2

Looking at the endo (f) and exo (f1) adduct peaks, or furan (f2) and maleimide (a1) reagents, the stoichiometry variation of endo-exo adducts and furan-maleimide reagent can be observed.

The temperature was plotted as function of the peak intensity with the methyl (s) of **M_2** as reference (Figure 6).

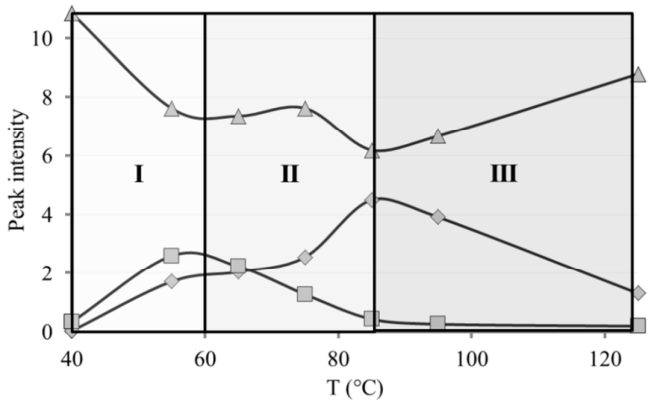


Figure 6: Proton peak intensity of adduct $A_{exo}F_5M_2$ ♦, $A_{endo}F_5M_2$■ and F_5 ▲of ^{1}H NMR analysis versus temperature

Figure 6 shows three distinct regions: the first one (**I**), from 40 to 60°C, where quantities of **$A_{endo}F_5M_2$** and **$A_{exo}F_5M_2$** increase and at the same time furfuryl acetate quantity decreases, corresponding to the Diels-Alder reaction; the second one (**II**), from 60 to 85°C, where the **$A_{endo}F_5M_2$** adduct quantity decreases and **$A_{exo}F_5M_2$** adduct amount increases, meaning that the retroDiels-Alder reaction of **$A_{endo}F_5M_2$** adduct occurred from T>60°C, and at the same time the creation (DA) of **$A_{exo}F_5M_2$** keeps going. In this region the quantity of **F_5** slowly increases until 75°C and then decreases until 85°C, which is due to the retroDiels-Alder of **$A_{endo}F_5M_2$** and the Diels-Alder of **$A_{exo}F_5M_2$** adduct, respectively. This transformation of endo to exo adduct is not a simple isomerization. These variations of each adduct ratio and the modification of **F_5** quantity show that prior to transformation from endo to exo form a retroDiels-Alder of the endo adduct occurs. In the third region (**III**), from 85 to 120°C, the quantities of **$A_{endo}F_5M_2$** and **$A_{exo}F_5M_2$** decrease while the **F_5** quantity increases. This result proves that the rDA of **$A_{exo}F_5M_2$** starts up to 85°C and whilst the retroDiels-Alder of **$A_{endo}F_5M_2$** keeps going.

From ^{1}H NMR, it is possible to determine, by 10 °C in our case, the rDA temperature. This method was applied to determine rDA temperature of a few furan derivatives. Results from Table 4 just allow showing the influence of R_2 substituent added on the furan derivatives. If the substituent is electro withdrawing (**AF_1M_2** to **AF_7M_2,** and **AF_9M_2**), DA and rDA are facilitated; on the contrary if the substituent is an electron attracting mesomeric effect (**AF_8M_2**) the DA reaction doesn't occurred as expected. The mesomeric form of the compound **F_8** blocks the doublet of the furan cycle which can not participate to the DA cyclization.

All those results show and confirm that the endo compound as to be mostly obtained to reach average unblocking temperatures.

Table 4: Variation of retroDiels-Alder temperature of exo and endo adduct as a function of blocking agents used with N-dodecylmaleimide (M_2)

Blocking Agent	retroDiels-Alder temperature(°C)	
	endo	exo
AF_2M_2	Between 55 and 65	Between 85 and 95
AF_4M_2		
AF_6M_2		
AF_7M_2		
AF_9M_2		
AF_1M_2	Between 65 and 75	
AF_3M_2		
AF_5M_2		
AF_8M_2	No Diels-Alder before 120°C	

Yet, these results do not allow determining unblocking kinetic which is an important aspect for the creation of material. That is why a complete study of some parameters effect on the retroDiels-Alder kinetic, i.e. temperature, presence of a nucleophile and the partners' backbone, has been carried out.

2.2 Influence of reaction parameters on the retroDiels-Alder kinetic

The aim of this part is to show the link between the Diels-Alder partners' backbone, the ratio endo/exo and the unblocking kinetic.

It is first important to increase the ratio in favor of the endo compound so as to obtain a system with an average unblocking temperature (70°C). According to starting diene and dienophile used for the Diels-Alder reaction, the endo or exo adduct could be favored. Some studies have been done about the influence of solvent and pressure on Diels-Alder conversion and enantiomeric yield. However, these works [48] showed that the increase of endo content is partially improved and principally depends on the partner backbone.

The use of a catalyst could also improve the ratio in favor of the endo adduct. For instance, some metallic catalysts have been described in the literature [49-51] and allow favoring this selectivity. However, Gandini and Belgacem[52] showed that the addition of a Brönsted acid or a Lewis acid as catalyst in presence of furan derivatives with a CH_2 in α position of the furan cycle, implies a polymerization of it. Moreover, the addition of a catalyst affects the endo/exo

ratio, but not the unblocking kinetic. In a nutshell, the use of a catalyst in our system is impossible.

It is well known that a decrease of the temperature during the protection (DA) increases the formation of the endo adduct and on the contrary, an increase of it implies an increase of the exo adduct formation. Thus, the Diels-Alder reaction has to be carried out at low temperature. Nevertheless, it can be stated the lower the temperature, the longer the blocking time and the longer the reaction time, the more the exo adduct is formed[34]. Therefore, it is significant to find the best compromise between temperature and blocking kinetic. In the project, the room temperature (20°C) has been chosen because it gives an endo/exo ratio largely in favor of the endo adduct and the protection kinetic (one week) is acceptable. Moreover, each diene/dienophile couple shows its own rDA temperature. It is therefore important to control if the unblocking temperature is not too high for the application. Indeed, the lower the temperature the better the material will be. Afterwards, the influence of the temperature on the unblocking reaction and the presence of nucleophilic reagent have been studied even if in all chemical reactions, the higher the temperature, the faster the kinetic.

Thus, work in ease conditions (20°C, without catalyst, long time) to obtain major endo adduct was chosen.

2.2.1 Kinetic study of retroDiels-Alder reaction at different temperature

The Diels-Alder reaction is a balance between a blocked and an unblocked form; it is thus expected to reach a plateau of the ratio during the retroDiels-Alder reaction. This ratio will depend upon the temperature.

To study the influence of the temperature, the compound **AF_1M_1** has been used and analyzed by ^{1}H NMR at three different temperatures (Figure 7).

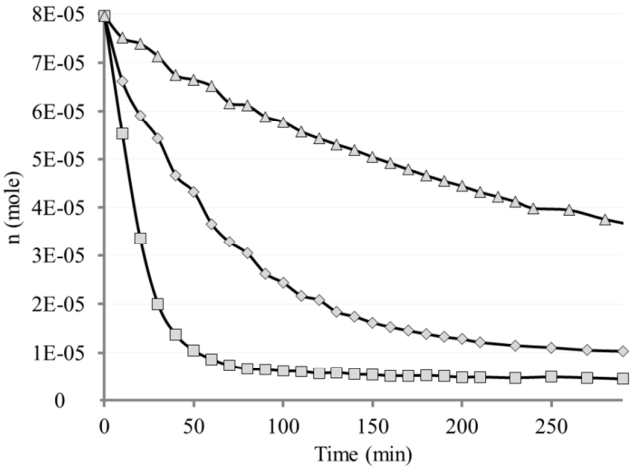


Figure 7: Evolution of $A_{endo}F_1M_1$ adduct mole number during the retroDiels-Alder reaction at different temperatures (60°C ▲, 70°C ♦ and 80°C ■) obtained by ^{1}H NMR.

Figure 7 shows that the higher the temperature the faster the mole number of $\mathbf{A_{endo}F_1M_1}$ decreases, which is coherent according to kinetic laws. Moreover, this analysis shows that, after 290min, the $\mathbf{A_{endo}F_1M_1}$ adduct still remains and the unblocking reaction is, as predicted, not complete. Indeed, even if the unblocking is the main reaction at high temperature, a small amount of both endo and exo adduct are, nevertheless, formed (Figure 10).The same results are observed for $\mathbf{A_{endo}F_1M_2}$ adduct.

The equilibrium constant K can be calculated at each temperature (Table 5) and plotting ln (n) versus f (t) allows obtaining straight lines with a slope being -αk (Figure 8), where $\alpha = 1$ in our case (equivalent number). The reaction has, thus, an order of one. The retroDiels-Alder reaction rate constant could be determined for each couple enabling to compare them (Table 6).

Table 5: Equilibrium constants for $A_{endo}F_1M_1$ and $A_{endo}F_1M_2$ at each temperature

T (°C)	60°C	70°C	80°C
$K_{AendoF1M1}$	$1{,}17.10^{-5}$	$1{,}17.10^{-4}$	$3{,}18.10^{-3}$
$K_{AendoF1M2}$	$2{,}37.10^{-4}$	$3{,}56.10^{-3}$	$3{,}58.10^{-3}$

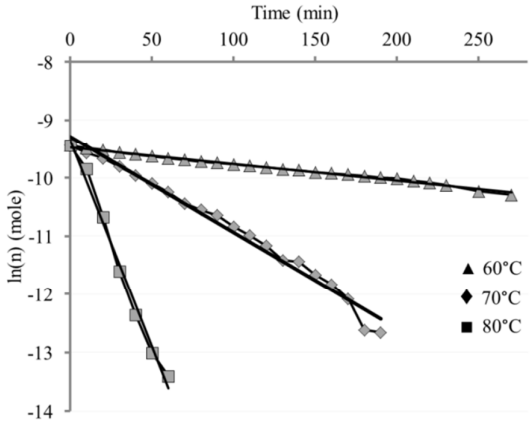


Figure 8: Rate constant determination of $A_{endo}F_1M_1$ adduct at different temperatures

The unblocking reactions were carried out at different temperatures. It is therefore possible to plot ln (k) versus f (1/T), from which the slope is equal to –Ea/R. Activation energy of the unblocking reaction of $\mathbf{A_{endo}F_1M_1}$ obtained is 156,7 kj.mol^{-1}.

Table 6: Summarize of all reaction rate constants obtained for $A_{endo}F_1M_1$

T (°C)	60	70	80
$k*10^3(min^{-1})$	2,8	17,1	71,1

Table 6 shows that the higher the temperature, the higher the rate constant. An increase of 10°C implies an approximately five times increase of the rate constant, which is significant.

With these rate values, activation parameters were determined from Eyring equation (Equation 2).

$$\log\left(\frac{k}{T}\right) = -8162{,}3 * \frac{1}{T} + 19{,}382$$

Equation 2: Eyring equation obtain from the plot f(1/T) = log(k/T)

The activation enthalpy ($\Delta H^{\ddagger}$) was estimated from the plot of logarithm of the quotient of rate k and temperature versus the reciprocal of temperature (1/T), while the entropie of activation ($\Delta S^{\ddagger}$) was determined from the intercepts with the y axe. The activation enthalpy found is 16.21 kcal/mol and the entropy activation is -8.6 cal/molK. This last value is far from typical value for concerted [2+4] cycloaddition reactions. For instance, Jasiński *et al*.[53] found that the reaction between cyclopentadiene and E-2-phenylnitroethene was -28.6 cal/molK activation entropy and 17.3 kcal/mol activation enthalpy. They proved that it was a concerted mechanism. In this case, the activation enthalpy and entropy values are close to the value obtained for the cycloaddition of 1,1-dimethoxy-1,3-butadiene and tetracyanoethylene, which is known to occur via zwitterionic mechanism ($\Delta H^{\ddagger}$ = 10.8 kcal/mol, $\Delta S^{\ddagger}$ = -6.2 cal/molK)[54]. For the retroDiels-Alder of $\mathbf{A_{endo}F_1M_1}$, it seems that a switterionic mechanism actually happened in the rate-determining step. Then, after unblocking reaction study, the elimination of one reagent after rDA has been investigated so as to verify if the reaction between a nucleophile and maleimide (Michael addition) is possible in situ from the rDA and if there is an impact on it's kinetic.

2.2.2 Influence of the presence of a nucleophile agent during rDA reaction

To do this study a thiolate is added in the mixture (a good nucleophile for the Michael reaction), which could reacts with the maleimide after unblocking reaction[55] and avoid a re-blocking of the maleimide's double bond. The Michael reaction shows a faster kinetic than the DA reaction kinetic, the maleimide should thus react with the thiolate preferentially[56] (Figure 9). It shows that the mole number of $\mathbf{A_{endo}F_1M_1}$ decreases faster in presence of thiophenol. As a consequence, the retroDiels-Alder reaction kinetic is faster when one of the partners is consumed at the same time as the unblocking reaction.

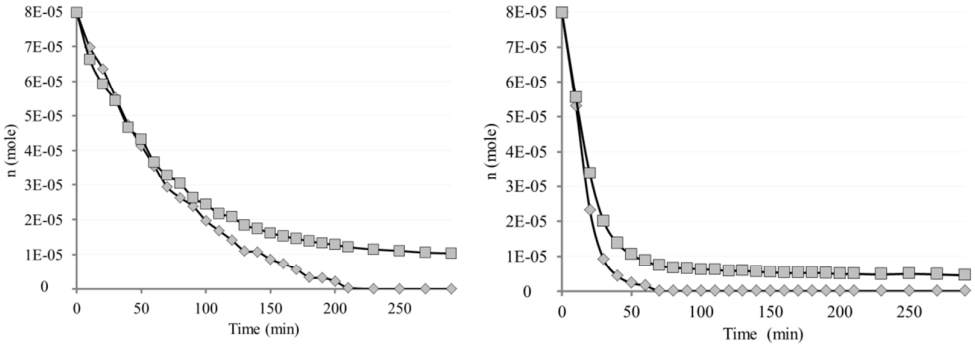


Figure 9: Mole number of $A_{exo}F_1M_1$ as function of time, obtained by ^{1}H NMR, during the retroDiels-Alder at 70°C (left) and 80°C (right) with ♦ or without ■ thiophenol

Moreover, during the unblocking reaction, the nucleophile enables consuming the unblocked maleimide and thus changing the balance on the unblocking reaction. Indeed, the retroDiels-Alder reaction is complete whereas, without a nucleophile, there is the balance reaction (Figure 10). This result confirms the assumption that the formation of exo adduct from the endo adduct is necessarily preceded by a retroDiels-alder of it. Indeed, with the thiophenol, no formation of exo adducts occurred, the maleimide's double bound is released and reacts, in situ, with the thiol avoiding it's creation. Moreover it was proved that the reaction of thiolate with the maleimide in situ of the unblocking reaction is possible.

All these results have allowed to set rules about the improvement of the unblocking reaction kinetic: increasing the temperature and consuming one of the partners after the unblocking reaction; and to confirm that a retroDiels-Alder occurs before the transformation from endo to exo adduct.

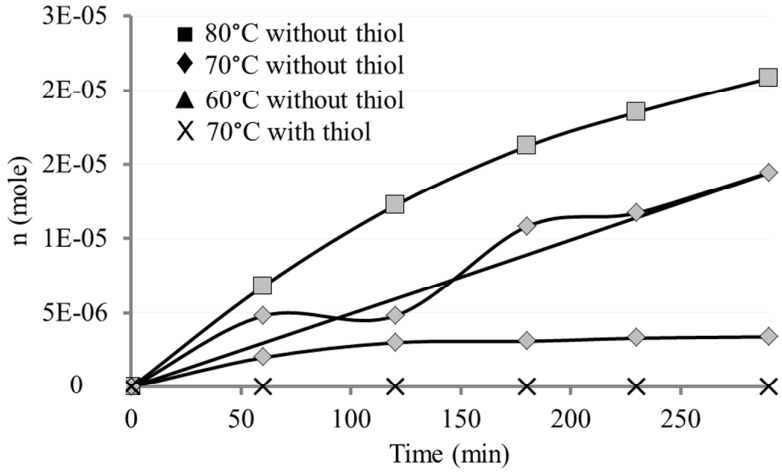


Figure 10: Mole number of $A_{exo}F_1M_1$ as function of time, obtained by ^{1}H NMR, during the retroDiels-Alder of $A_{endo}F_1M_1$ at different temperatures

This work has been done at the same concentration and, as it is known, the kinetic depends on the concentration of all starting materials. So the influence of the ratio and the concentration on the reaction kinetic has been investigated.

2.2.3 Influence of the endo/exo ratio and of the starting material concentration

The influence of the ratio between endo and exo adduct on the unblocking reaction of $\mathbf{A_{endo}F_1M_1}$ was studied by ^{1}H NMR with a constant concentration of starting materials ($\mathbf{A_{endo}F_1M_1}$/$\mathbf{A_{exo}F_1M_1}$) and a varying ratio (Figure 11). The variation of the peak intensity of H_f protons of $\mathbf{A_{endo}F_1M_1}$ adduct at 70°C was plotted against time.

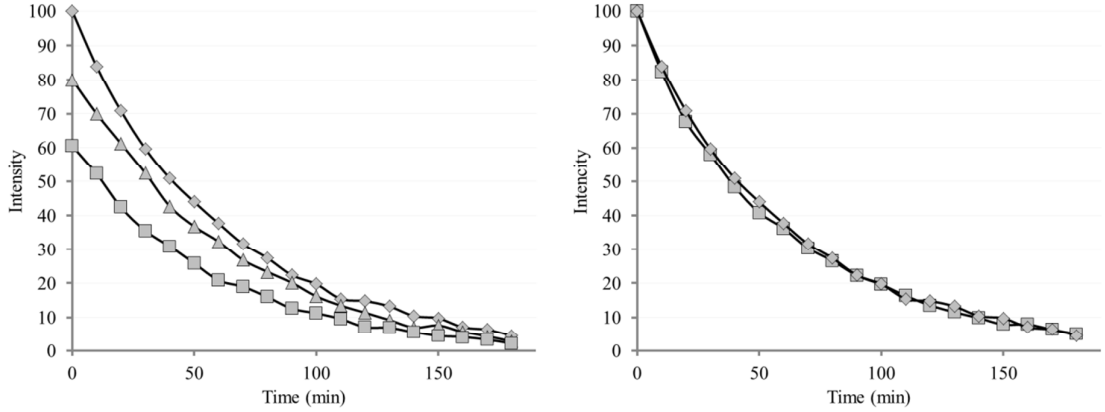


Figure 11: Effect of the endo/exo ratio (100% ♦, 77% ▲, 61% ■) (left) and the concentration (30mg/ml ♦ and 50mg/ml ■) (right) on the rDA kinetic at 70°C

To compare all three curves of the Figure 11, as before, the rate constants (k) are used. The results show that whatever the ratio, the rate constants (k) are all equal to 0,017 min^{-1}. As a conclusion, the ratio has no effect on the unblocking reaction kinetic. Also, with or without exo adduct in the mixture, the retroDiels-Alder reaction kinetic remains the same.

Afterwards, the variation of the $\mathbf{A_{endo}F_1M_1}$ adduct concentration on the rate constant (k) was studied (Figure 11) and shows that the kinetic is the same whatever the starting concentration. The reaction kinetic is concentration dependent, and it seems less probable that the concentration hasn't got an influence on the unblocking kinetic. In this case, the unblocking reaction is not affected by the concentration because this last is too low.

In this study, only the compound $\mathbf{AF_1M_1}$ was used. However, the unblocking reaction should be dependent on the couple furan derivatives/maleimide used for the Diels-Alder reaction. Thus, in this last part, the influence of substituents R_1 of the maleimide and R_2/R_3 of the furan derivatives on the Diels-Alder reaction was investigated.

2.2.4 Influence of the couple furan derivatives/maleimide

The product used is significant for the Diels-Alder reaction. Indeed, the addition of an electron donating mesomeric substituent on the diene and the addition of an electron attracting mesomeric substituent on the dienophile, increase considerably the blocking reaction kinetic and the creation of endo adduct.

Several furan and maleimide derivatives were thus synthesized and used to determine the influence of substituent added on diastereoselectivity and on rDA kinetic. It will allow deducing rules about blocking reaction between furan and maleimide derivatives.

Yields and ratio of Diels-Alder adducts were determined by ^{1}H NMR. All results are summarized in Table 2/Table 3 and show that the backbone of R_1, R_2 and R_3 has an influence on the ratio. Indeed, endo adducts are favored by the presence of electro giving substituent on maleimide (compound **M_5**) and by electron donating mesomeric substituent (played by the oxygen atom on the furan backbone) coupled with electro withdrawing substituent in α position on the furan cycle (compound **F_7**). Furan/maleimide choice couples enable favoring or disfavoring one of the adduct and, as a consequence, to choose the best one depending on its application. In our case, the couple **F_7/M_5** should be the best to obtain only the endo adduct and, thus, to obtain an average unblocking temperature.

On the one hand, to study the influence of the blocking agent (furan derivatives, **F**) on unblocking reaction kinetic of endo adduct, an ^{1}H NMR monitoring was performed on the N-methylmaleimide (**M_1**) blocked with all furan derivatives. On the other hand, the influence of maleimide on unblocking reaction kinetic of the endo adduct has been studied by ^{1}H NMR monitoring on each maleimide blocked with furfuryl acetate (**F_1**) (Figure 12).

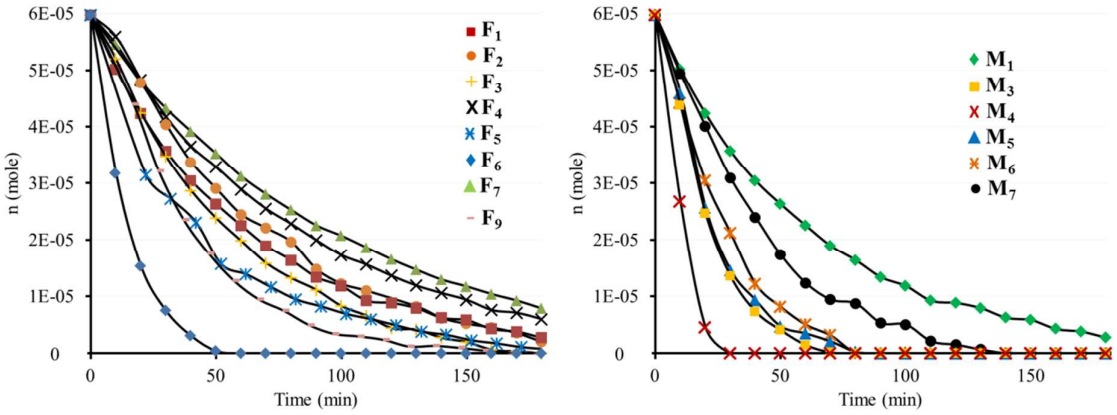


Figure 12: Influence of the N-methylmaleimide (M_1) blocking agent with furan derivatives (left) and of every maleimide blocked with furfuryl acetate (F_1) (right) on unblocking reaction kinetic of endo adduct at 70°C

Since the exo adduct has no influence on unblocking reaction kinetic, it was not necessary to purify them. Adducts mole numbers are, thus, used. The rate constant for each blocking

agents used on $\mathbf{M_1}$ and each maleimide blocked with $\mathbf{F_1}$ are summarized in the Table 7 below ($\mathbf{M_2}$ has not been studied because the required amount of product for the kinetic was not fully soluble in 0.6mL of $DMSOD_6$).

Finally, the more the substituents R_2 and R_3 of the blocking agent are electro withdrawing, the slower the retroDiels-Alder kinetic. Moreover the more R_1 on maleimide is attracting mesomeric, the faster the unblocking reaction kinetic. However, the higher the ratio is in favor of endo adduct, the slower the retroDiels-Alder kinetic. It implies that the higher endo adduct is obtained, the higher it's thermodynamically stable and thus leads to a slower kinetic. Nevertheless, there is no proportional behavior between unblocking kinetic and the ratio endo/exo.

Table 7: Summarize of rate constant k for each blocking agent used on N-methylmaleimide (M_1) and each maleimide blocked with furfuryl acetate (F_1)

Blocking agent	$\mathbf{F_1}$	$\mathbf{F_2}$	$\mathbf{F_3}$	$\mathbf{F_4}$	$\mathbf{F_5}$	$\mathbf{F_6}$	$\mathbf{F_7}$	$\mathbf{F_9}$
$k*10^3$ (min^{-1})	16,3	17,5	22,3	12,8	21,9	74,1	11,1	30,5
Maleimide	$\mathbf{M_1}$	$\mathbf{M_3}$	$\mathbf{M_4}$	$\mathbf{M_5}$	$\mathbf{M_6}$	$\mathbf{M_7}$	/	/
$k*10^3$(min^{-1})	16,3	61,4	129,1	50,0	29,7	43,0	/	/

3 Experimental part

3.1 Materials and reagents

Furan derivatives blocking agents were obtained from commercial sources or synthesized in laboratory. furfuryl acetate ≥98%, , 2-(2-furyl)-1,3-dioxolane 98%, propionate furfuryl ≥98%, thiophenol 97%, maleic anhydride 99%, 1-methoxy-2-propylamine 95%, zinc bromide :≥98%, hexamethyldisilazane>99%, anhydrious sodium sulfate, aniline ≥99,5%, *p*-anisidine ≥99%, 4-nitroaniline ≥99%, N-dodecylamine ≥98%, 2-methoxyethylamine ≥99%, alcohol furfuryl 98%, 2-furoyl chloride 95%, triethylamine ≥99%, cyclohexanecarbonyl chloride 98%, 3,5,5-trimethylhexanoyl chloride 98%, benzoyl chloride 99% and pivaloyl chloride 99%, 5-methylfuran 99%, 5-methyl-2-furaldehyde 98% were purchased from Sigma-Aldrich. N-methylmaleimide 97% and 5-hydroxymethyl-2-furaldehyde 98% were purchased from ABCR and used without purification.

3.2 Product Characterization

All products were characterized by nuclear magnetic resonance of protons (^{1}H NMR) and carbon (^{13}C NMR). Measurements have been done thanks to a spectrometer Brucker Aspect 400MHz. Deuterium solvent used depends on the product and will be detailed in each case.

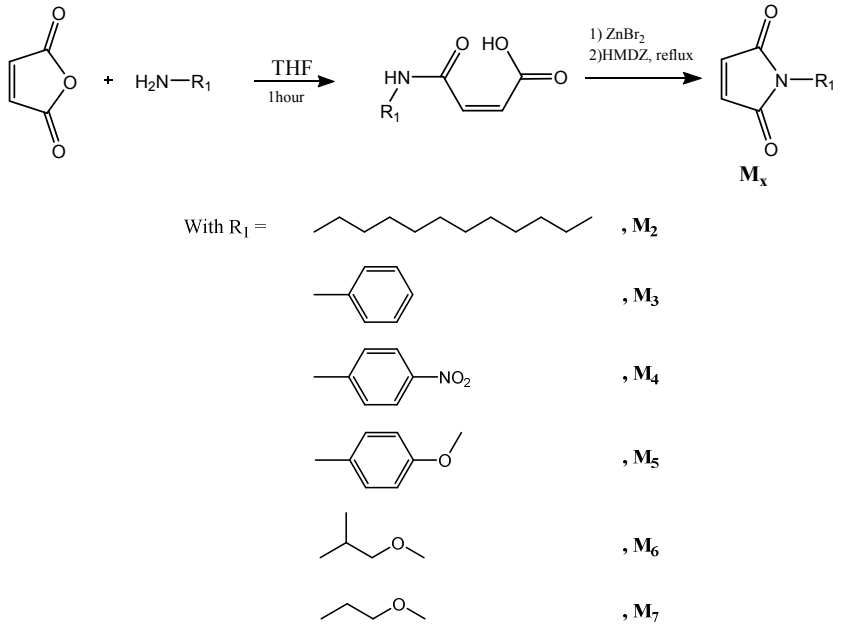
Chemical shifts are given in (ppm) with an s for singlet, a d for doublet, a t for triplet and an m for multiplet.

Differential Scanning Calorimetry (DSC) analyses were carried out on a NETZSCH DSC200 calorimeter. Cell constant calibration was performed using indium, n-octadecane and n-octane standards. Nitrogen was used as the purge gas.

Informatics representation and calculation of $\mathbf{A_{endo}F_1M_1}$ were done with MOPAC 2012 software (quantic semi-empirical calculation) and AM1 methods (geometrical optimization with the convergence criteria "precise").

3.3 Synthesis of maleimide

The way used to synthesize maleimide model is presented in Scheme 2 [57].



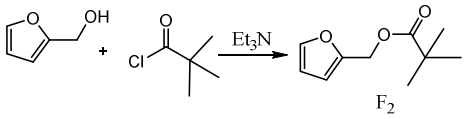
Scheme 2: Synthesis of maleimide model (M_x)

Maleic anhydride (1.1eq/amine function) is reacted with amine in THF (4ml/g) during 1 hour. Amine is added drop by drop. Then $ZnBr_2$ (1.4eq/amic acid function) is added under nitrogen. After solubilization, the mixture is heated at 40°C, and then HMDZ in THF (1.4eq/amic acid function) is added drop by drop during 30 minutes. After total addition, the temperature is raised to 70°C for 4 hours. At the end of the reaction the mixture is filtered off and the solvent is evaporated under low pressure. Several purifications have been done and will be specified for each product.

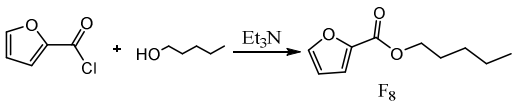
3.4 Synthesis of furan derivative

Three different ways for blocking agents synthesis have been used: the first one (**way 1**) using alcohol furfuryl (Scheme 3), the second one (**way 2**) using furoyl chloride (Scheme 4) and the third one (**way 3**)[58] using aldehydes (Scheme 5).

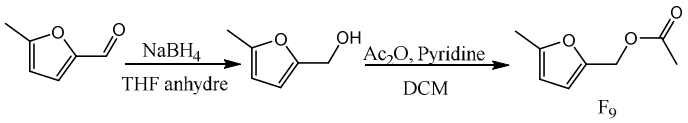
All substituents R_2/R_3 have been chosen for their electronegativity and their hindering (Figure 13).



Scheme 3*: *Example of synthesis of alcohol furfuryl derivatives (way 1)



Scheme 4*: *Synthesis of furoyl chloride derivative F_8 (way 2)



Scheme 5: Synthesis of blocking agent F_9 using the aldehyde (way 3)

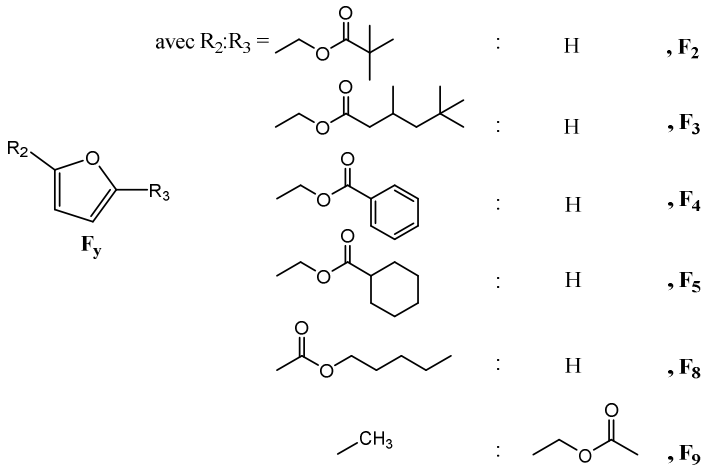


Figure 13: All furan derivatives (F_y) synthesized (s)

For both **way 1** and **way 2**: an Acid chloride (1.3eq/alcohol function) is solubilized in dry dichloromethane (1ml/g of product). Then triethylamine (1.3eq) is added under nitrogen drop by drop to the mixture. Amine is added drop by drop. The alcohol (1eq) is added drop by drop, under nitrogen, at 0°C during 15 minutes. The reaction mixture is then heated at 40°C during 5 hours. Then the mixture is filtered off and the solvent is evaporated under low pressure. Several purifications have been done and will be specified for each product.

For **way 3**: an aldehyde (1eq) is solubilized in dry THF (3ml/g of product) at 0°C, under nitrogen. Then sodium borohydride (2eq) is slowly added during 10 minutes. After 2 hours

the reaction mixture is neutralized with HCl (2N). The product is extracted with ethyl acetate solvent. The organic layer is dried with anhydrous magnesium sulfate and the product is crystalized at 0°C. A pale yellow powder is obtained.

3.5 Synthesis of Diels-Alder adduct

Maleimide **M** (1eq) is solubilized in the solvent (DCM for $\mathbf{M_1}$ or THF for $\mathbf{M_2}$) (2ml/g of product). Then the furan derivative **F** (1.1eq) is added. The reaction mixture is stirred for two weeks at 23°C.

3.6 Characterization of Diels-Alder and retroDiels-Alder reaction

3.6.1 By isothermal ^{1}H NMR

In an NMR tube, all reactants for Diels-Alder synthesis are mixed. The solvent used is DMSO D_6, because of its high boiling point at 190°C, which enables to do thermal reaction directly in the NMR tube. All spectrums are saved every 5 minutes with 32 acquisitions, in automatic mode, during 1 hour by temperature stage (40, 55, 65, 75, 85, 95, 105,115 and 125°C).

3.6.2 By DSC

In a DSC capsule (sealed when solvent is used), the Diels-Alder adduct, solubilized or not in DMSO, is weighted (between 5 and 10 mg). For the characterization, for blocking or unblocking reaction, the analysis is a step up from 20°C to 150°C, 2°C/min, then a step down to 20°C, 2°C/min. The cycle is repeated twice. For the characterization of the unblocking reaction in solvent, the analysis is a step up, 10°C/min, until 70°C, and then the capsule is isothermally heated at 70°C during 4 hours and then a step down to 20°C.

3.6.3 Characterisation of retroDiels-Alder kinetic by isothermal ^{1}H NMR

In an NMR tube, the Diels-Alder adduct is solubilized in 0,6ml of $DMSOD_6$. For the study in presence of a nucleophile, a drop of thiophenol and DABCO are added. Then the tube is placed in the NMR and is heated at constant temperature (60°C, 70°C, 80°C) during 5 hours. A spectrum is saved every 5 minutes with 32 acquisitions, in automatic mode.

4 Conclusion

As a conclusion, this study showed a way to increase the ratio endo/exo in favor of endo adducts in Furan derivatives/maleimide system: the Diels-Alder reaction has to be carried out at low temperature; electro withdrawing R_2 and R_3 substituents, and electron donating R_1

substituents should be favored. Moreover, the unblocking reaction time could be adjustable with substituents added on Diels-Alder partners. The unblocking reaction is favored with electro withdrawing R_2 and electro attracting mesomeric R_1 substituents. If, in the mixture, there is also a nucleophile (thiol), the unblocking reaction is faster.

This study enabled to re-demonstrate general points about the Diels-Alder reaction already known, as well as to show the link between external factor and partners backbones with the ratio endo/exo and the retroDiels-Alder kinetic. Consequently, it is possible to create a system with a control of the reaction temperature, a control of the unblocking reaction kinetic and a system which could reacts on demand with a nucleophile (release of the maleimide reactive double bond by rDA and reaction, in situ, with nucleophile). Thanks to this study, a future publication will aim at preparing multifunctional products so as to create new type controlled cross-linked materials containing Diels-Alder adducts and nucleophile where it is possible to trigger the reaction after stimuli (submitted).

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6 References

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STUDY OF THE DIELS-ALDER AND RETRO-DIELS-ALDER REACTION BETWEEN FURAN DERIVATIVES AND MALEIMIDE FOR THE CREATION OF NEW MATERIALS

Graphical Abstract