PHOTOCHEMICAL DIMERIZATION IN SOLUTION OF HETEROCYCLIC SUBSTITUTED ALKENES BEARING AN ELECTRON WITHDRAWING GROUP

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Abstract – *The photochemical dimerization in solution of heterocycle substituted alkenes bearing electron withdrawing groups is reported. The reactions occurred both in the singlet and in the triplet states showing good regio- and stereoselectivities. The regioselectivity can be explained assuming that the dimerization reaction is frontier orbitals controlled. The stereoselectivity can be explained assuming the formation of the most stable isomers.*

The photochemical dimerization of cinnamic acid has been known over 80 years.[1,2] Cinnamic acid (**1**), irradiated in the solid state, gave the corresponding photodimers depending on the crystal form of the starting material: the metastable β-form is reported to yield β-truxinic acid (**2**), while the stable α-form gave α-truxillic acid (**3**) (Scheme 1).[3-7]
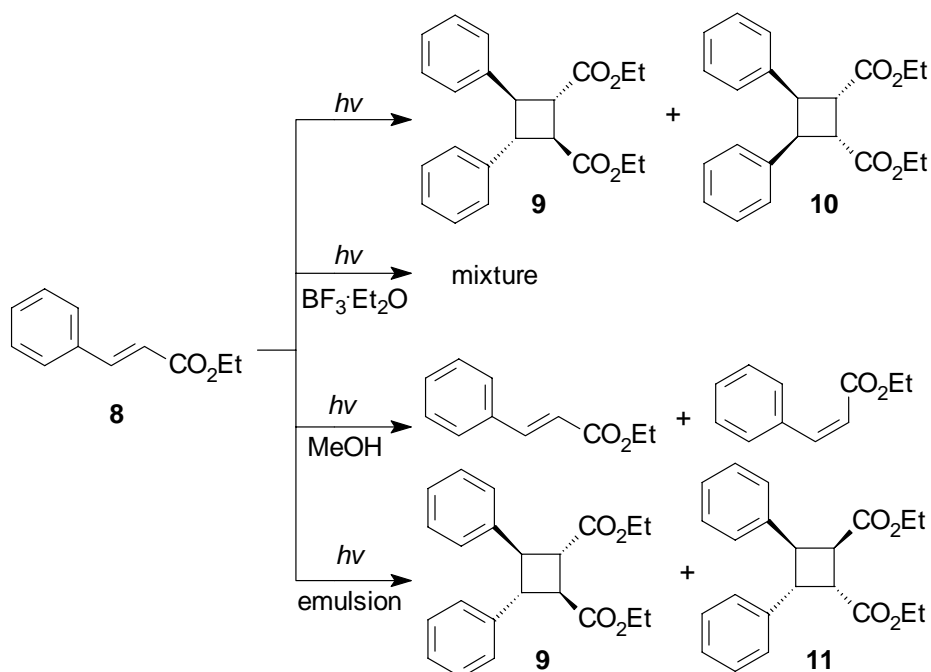
Scheme 1
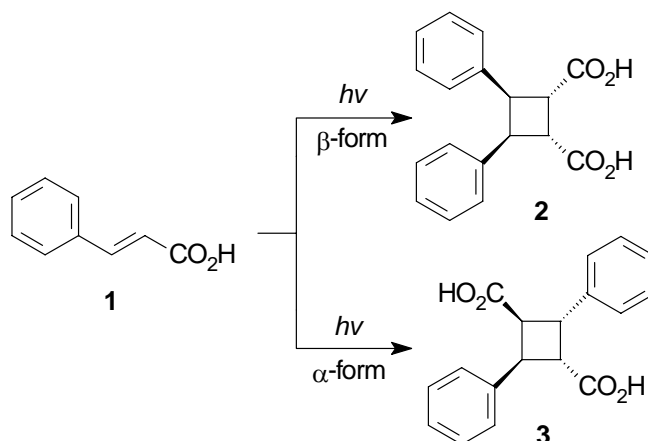
This type of reaction can also be performed on 3-(2-furyl)acrylic acid (**4**) or on 3-(2-thienyl)acrylic acid (**6**) to give the corresponding photodimers (**5**) and (**7**) if the irradiation is performed in the solid state (Scheme 2).[8] It is noteworthy that these reactions need 30 and 20 days of irradiation, respectively, to give the products. Irradiation of **4** and **7** in solution (MeOH) showed only *E-Z* isomerization of the starting materials.[9]

Scheme 2
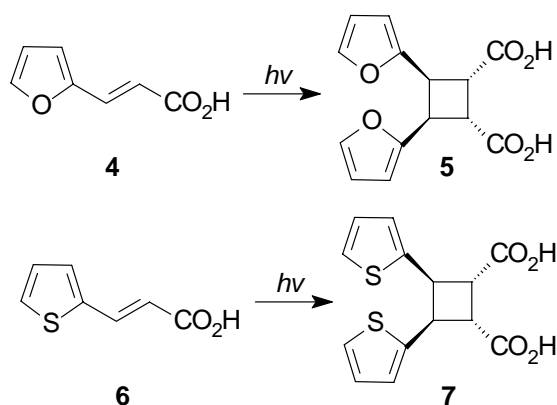
While the reactivity of cinnamic acid is well defined, the reactivity of the esters is more complex. Irradiation of liquid ethyl cinnamate (**8**) furnished a mixture of two compounds (**9**) and (**10**) in 55 and 25% yields, respectively (Scheme 3).[10,11]

Scheme 3

When the reaction was performed in a mixture of water (82.1%), cyclohexane (3.2%), butanol (9.8%), and sodium dodecyl sulfate (4.9%), an 8:2 mixture of *trans*-diesters (**9**) and (**11**) was obtained (Scheme 3).[12] On the other hand, irradiation in methanolic solution did not furnish any cyclodimerization product, giving instead only *E-Z* isomerization,[13] while irradiation in the presence of BF$_3$ furnished a mixture of seven dimers (Scheme 3).[14,15] However, the application of this methodology to methyl 3,4-dimethoxycinnamate failed.[16] 3,4-Dimethoxycinnamic derivatives can be dimerized only in the presence of cyclodextrin.[17] Recently, we found that methoxy-, dimethoxy-, and trimethoxycinnamate esters can be dimerized in acetonitrile both in the presence or in the absence of a triplet sensitizer.[18]

In this review we account for our work in the field of photochemical dimerization of heterocyclic alkenes in solution.

1.   Dimerization of acrylic esters

Irradiation of methyl 3-(2-furyl)acrylate (**12**) in acetonitrile in the presence of benzophenone as sensitizer furnished a mixture of two compounds (**13** and **14**) in 61 and 27% yields, respectively (Scheme 4).[19,20] The furyl acrylates (**15**) and (**16**), with a methyl group respectively in an α-position to the carboxylic ester and in an α-position on the furan ring, showed different behaviors. While compound (**15**) did not give any photodimer, its isomer (**16**) furnished only the photodimer (**17**), in 22% yield (Scheme 4).[19]

Scheme 4
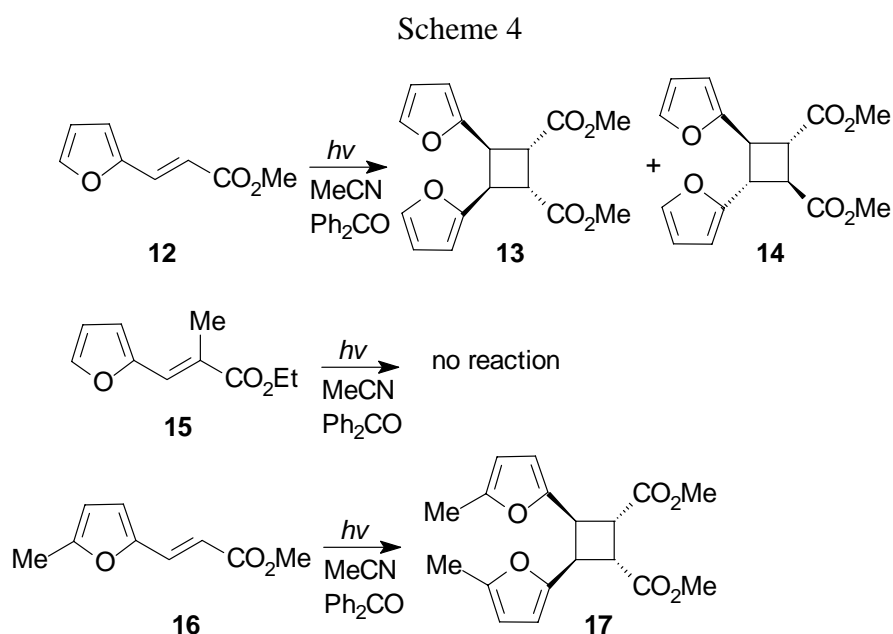
We did not observe the formation of products of type (**14**). The presence of substituents on the double bond seems to be incompatible with photodimer formation while, unexpectedly, substitution on the furan ring also depresses the reactivity of the double bond.

Direct irradiation of **12** in an immersion apparatus equipped with a Pyrex filter allowed us to obtain a *Z-E* photostationary equilibrium.[21] In different solvents (acetonitrile, methanol, ethyl acetate, ethanol, and benzene) we observed the formation of 25% *Z* isomer in the reaction mixture but no formation of any dimerization product. *Z-E* isomerization is a very fast reaction. The UV spectrum of **12** showed a strong absorption band at λ 299 nm. When the substrate was irradiated with a mercury lamp without filter for a few seconds, shift of the peak at λ 299 nm to λ 302 nm was observed. This bathochromic shift is maintained even after prolonged irradiation. Laser flash photolysis experiments showed that direct irradiation of **12** in acetonitrile, ethanol, and benzene did not produce any transient state using both 308 and 347 nm excitation. The only photoproduct obtained by UV irradiation of **12** in benzene, ethanol, and acetonitrile was the *Z* isomer; the photoisomerization quantum yield value (0.4 in benzene at λ_{exc} 313 nm) evidences that *trans→perp* rotation is the main decay process of the excited states of **12**. Since there is no evidence of triplet state population under these experimental conditions, it strongly suggests that only the lowest singlet state is involved in the photoisomerization process.

We carried out the dimerization reactions irradiating a 8.2 x 10^{-2} M solution of **12** in the presence of 3.43 x 10^{-3} M benzophenone in a Rayonet chamber reactor equipped with a Pyrex filter with lamps bearing a spectral output at 350 nm.[21] The *Z* isomer rapidly (10 min) reached 0.65 x 10^{-2} M concentration and maintained this concentration during all our experiments. Dimer formation followed a zero order kinetics in agreement with a sensitized reaction. We obtained $k = 1.38$ x 10^{-3} M s^{-1}. The zero order kinetics strictly depends on the benzophenone concentration. In fact, experiments in benzene at different benzophenone concentrations gave a linear function.[21]

Using laser flash photolysis apparatus in acetonitrile, the triplet of benzophenone ($E_T = 69$ kcal mol^{-1}) is efficiently quenched by **12**, which reduces its lifetime from ca. 4 μs to < 40 ns. In the meantime, a new transient species appears in the 380 nm region and decays with a lifetime of 140 ns (first-order kinetic). Since the same transient is sensitized by xanthone ($E_T = 74$ kcal mol^{-1}) and thioxanthone ($E_T = 65$ kcal mol^{-1}) it is assigned to the lowest triplet state of **12**. Its fast decay is in agreement with an efficient *trans→perp* rotation. In ethanol, irradiation of benzophenone produces a triplet which has a much shorter lifetime (τ_T *ca*. 100 ns) and a ketyl radical ($\tau_{\frac{1}{2}}$ *ca*. 50 μs). Addition of **12** quenches benzophenone triplet to a τ_T < 30 ns with concomitant formation of a lowest excited triplet state of **12** at 380 nm. The decay of the ketyl radical is not influenced by the concentration of **12** even if its absorption is significantly reduced.[21]

In conclusion, it seems that furylacrylate dimerization reaction occurs in the triplet state of the molecule and that this triplet state is obtained *via* energy transfer from benzophenone.

We have to answer to the question regarding the observed regio- and stereoselectivities of the reaction. We have to explain the reason of the formation of only two isomers from eleven possible dimers.

In order to explain the formation of only head-to-head dimers we have examined the possibility of frontier orbital control in the stereochemical behavior of methyl 3-(2-furyl)acrylate. We have estimated the HOMO and LUMO energy for this compound by using the AM1-UHF semiempirical method and the results are collected in Table 1.

Clearly, the best interaction occurs between the LSOMO of the excited triplet state and the HOMO of the fundamental singlet state. The LSOMO for the triplet state of **12** and the HUMO for the fundamental singlet state of the same molecule are depicted in Figure 1.

Table 1 - HOMO and LUMO for methyl 3-(2-furyl)acrylate.

Electronic State	HOMO (eV)	LUMO (eV)	LSOMO (eV)	HSOMO (eV)
S_0	- 9.20	- 0.83		
T_1			- 6.22	-3.91
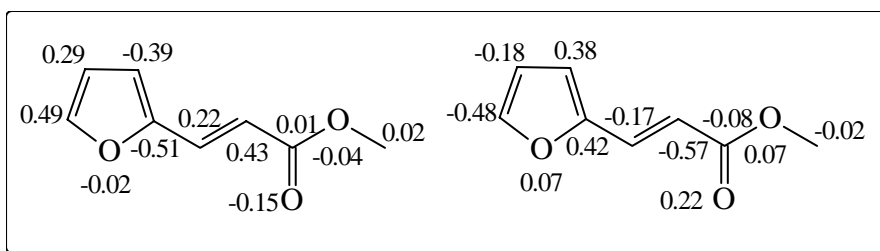
Figure 1 - HOMO of S_0 and LSOMO of T_1 state of **12**.

We can see clearly that, in this case, we have the total superposition between the molecules of the reagents. These data can explain the formation of only head-to head dimers, because, in the case of head-to-tail dimers, the same superposition is not allowed. While the frontier orbitals allow us to explain regiochemical behavior of the photochemical reaction, the stereochemistry of the reaction can not be explained on the basis of this theory.
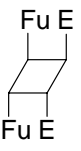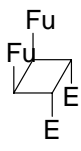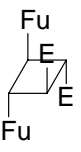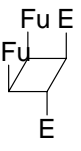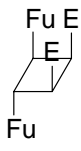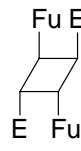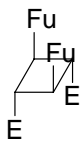
Recently, studying the photodimerization reaction of methyl cinnamate, molecular mechanics calculations showed that the relative stabilities of the dimers are in the order δ (27.12 kcal mol^{-1}) > ξ (28.81 kcal mol^{-1}) > μ (29.48 kcal mol^{-1}) > β (31.98 kcal mol^{-1}). δ-Truxinate ester is the dimer (**9**) while the β-isomer is the dimer (**10**).[22] In our case, we performed molecular mechanics calculations by using MM+ program in HyperChem packet. In this case we observed a completely different trend. In fact, the dimer (**13**) showed a steric energy of 63.86 kcal mol^{-1}, while the dimer (**14**) showed a value of 52.04 kcal mol^{-1}. We observed very different values in the steric energy in comparison with those reported for truxinate esters and these values were higher than those previously reported for the cinnamate dimers.[22] In particular the

bending energy was the main cause of this difference. This effect is probably due to the presence of the more polar furan ring in the molecule.

Nevertheless, on the basis of this calculations, the main product of the photochemical dimerization of **12** is less stable than the other product. Then, this approach does not allow us to solve the problem of the stereochemistry of the dimerization reaction.

In order to solve this problem, we calculated the electronic total energy for all the possible dimers. Calculations were performed by using, also in this case, AM1-UHF semiempirical method. The data are collected in Table 2.

**Table 2** - Total electronic energy of dimers of methyl 3-(2-furyl)acrylate

| Substrate[a]	-E (kcal mol^{-1})	Substrate[a]	-E (kcal mol^{-1})	Substrate[a]	-E (kcal mol^{-1})
Fu E / Fu E	96448	Fu / Fu E / E	96482	Fu E / E Fu	95265
Fu E / E / Fu	95472	Fu E / Fu E	96235	Fu / E / E Fu	96268
Fu E / Fu / E	96461	Fu E / E / Fu	96465	Fu E / E Fu	96277
Fu / E Fu / E	96272	Fu / Fu / E / E	96472	

a) Fu = 2-Furyl, E = CO$_2$Me

We can see that head-to-head dimers are usually more stable than head-to-tail isomers. This could be second justification of the regiochemical control of the reaction. Furthermore, within head-to-head dimers, the more stable dimers are the obtained ones. Different stability between these two dimers accounts for the different yields observed.

We wanted to verify the effect of a change in the nature of aromatic ring on the reactivity: for this purpose we used the thienyl derivative (**18**). The thienyl derivative (**18**) gave a mixture of two cyclobutane derivatives (**19**) and (**20**) in 1:1 ratio but we obtained this compounds with an overall yield of

25% (Scheme 5).[19] In this case, the best interaction can be obtained between LUMO of the S_0 and the HSOMO of T_1. However, the superposition of the orbitals is not complete and this fact could explain the low reactivity observed.[23]
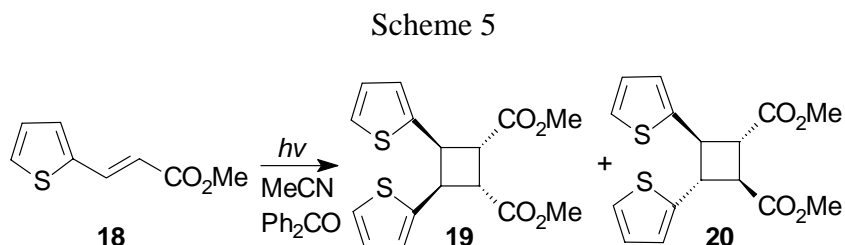
Scheme 5

The irradiation of methyl and ethyl urocanates (**21a-b**) led to the formation of a mixture of two dimers (**22a-b**) and (**23a-b**) (Scheme 6).[24]

Scheme 6

a: R = CH$_3$
b: R = C$_2$H$_5$
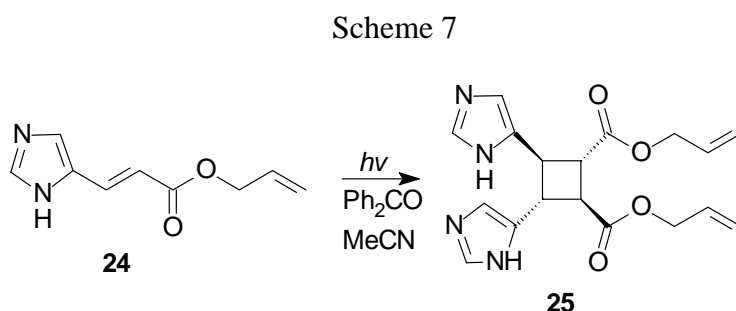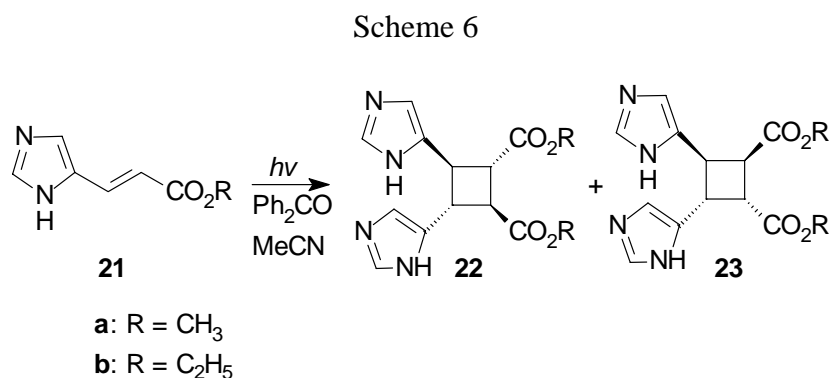
Scheme 7

The irradiation of allyl urocanate (**24**) gave an interesting result. In this case the above described regio- and stereoselectivities was enhanced. In fact, we observed the selective formation of only one dimer (**25**) (Scheme 7).[24]

These experimental data allow us to draw a conclusion. In spite of the previous reported data where only the *Z-E* isomerization of urocanate was described, the presence of benzophenone can sensitize the dimerization of urocanate esters.

Furthermore, we have to note that the reaction showed a high regio- and stereochemical controls. The high stereoselectivity here observed in particular in the case of the dimerization of compound (**24**) was not described before.

The regiochemical behavior can be explained assuming frontier orbital control of the reaction. We estimated the HOMO and the LUMO energies for the compound (**21a**) by using PM3-RHF-CI semiempirical method and the results are collected in Table 3 . In fact, the best interaction occurs between the LSOMO of the excited triplet state and the HOMO of the ground singlet state. The L and HSOMOs for the triplet state and the HOMO and the LUMO for the ground singlet state of the same molecule are depicted in Figure 2.

Table 3 - HOMO and LUMO of imidazolylacrylic derivatives

Compound	Electronic state	HOMO (eV)	LUMO (eV)	LSOMO (eV)	HSOMO (eV)
21a	S_0	- 9.152	- 1.004		
	T_1			- 6.635	- 3.646
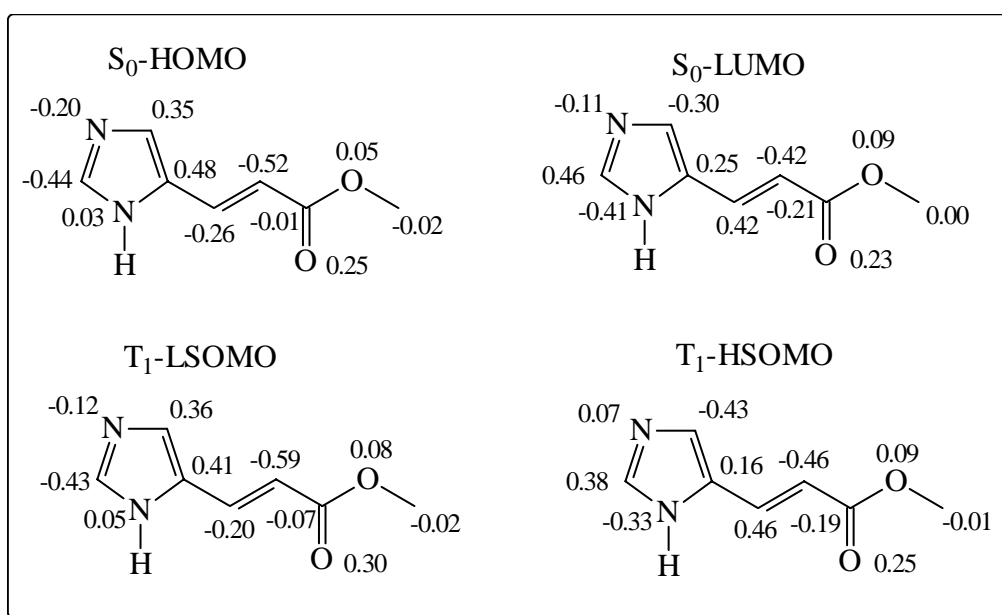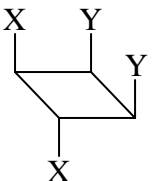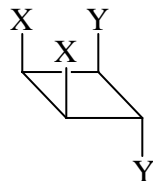
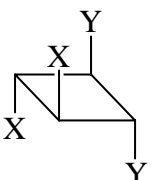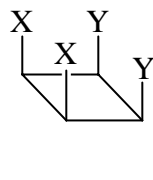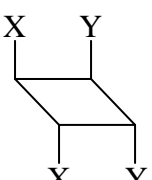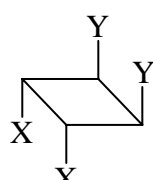**Figure 2** - LSOMO and HSOMO of T_1 and HOMO and LUMO of S_0 of compound (**21a**).

Therefore, we can see that we have a total superposition between both LSOMO/HOMO and HSOMO/LUMO of the reagents. These data are in agreement with the exclusive formation of head-to-head dimers. The stereochemical behavior of the dimerization of methyl urocanate can be explained calculating the heat of formation for all the possible head-to-head dimers. Calculations were performed by using AM1 semiempirical method. The data are collected in Table 4. We can see that the more stable

dimers are the obtained ones. Furthermore, different stability between the dimers accounts for different yields observed.

Table 4 – Heat of formation of all the head-to-head dimers of imidazolylacrylates

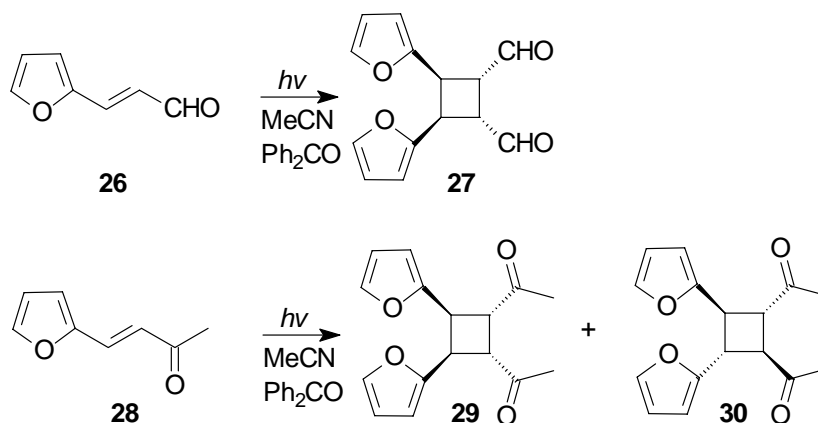| Dimer	Heat of Formation (kcal mol^{-1})		Dimer	Heat of Formation (kcal mol^{-1})	
	Methyl ester	Allyl ester		Methyl ester	Allyl ester
(dimer structure)	-52.42	-8.89	(dimer structure)	-53.37	-12.85
(dimer structure)	-61.74	-16.69	(dimer structure)	-46.54	-4.21
(dimer structure)	-54.64	-5.48	(dimer structure)	-48.92	-7.71

X = 1H-imidazol-4-yl, Y = CO$_2$R

In the case of the allyl ester, the compound which showed the highest stereoselectivity, the data collected in Table 4 are in agreement with the formation of the compound (**25**): in fact, it is the more stable dimer. In this case, the dimer corresponding to the compound (**23a**) was not obtained, and the data reported in Table 4 are in agreement with this result: in fact, this dimer showed ΔH_f = -5.48 kcal mol^{-1} and this value is high if compared with the ΔH_f of the compound (**25**) (-16.69 kcal mol^{-1}).

Furthermore, we did not observe the formation of a dimer with ΔH_f = -12.85 kcal mol^{-1}. In this case, the photochemical behavior of the substrate seems exclude the formation of dimers with a *cis* relationship between two imidazolyl rings. On the basis of our results we can not explain this selectivity.
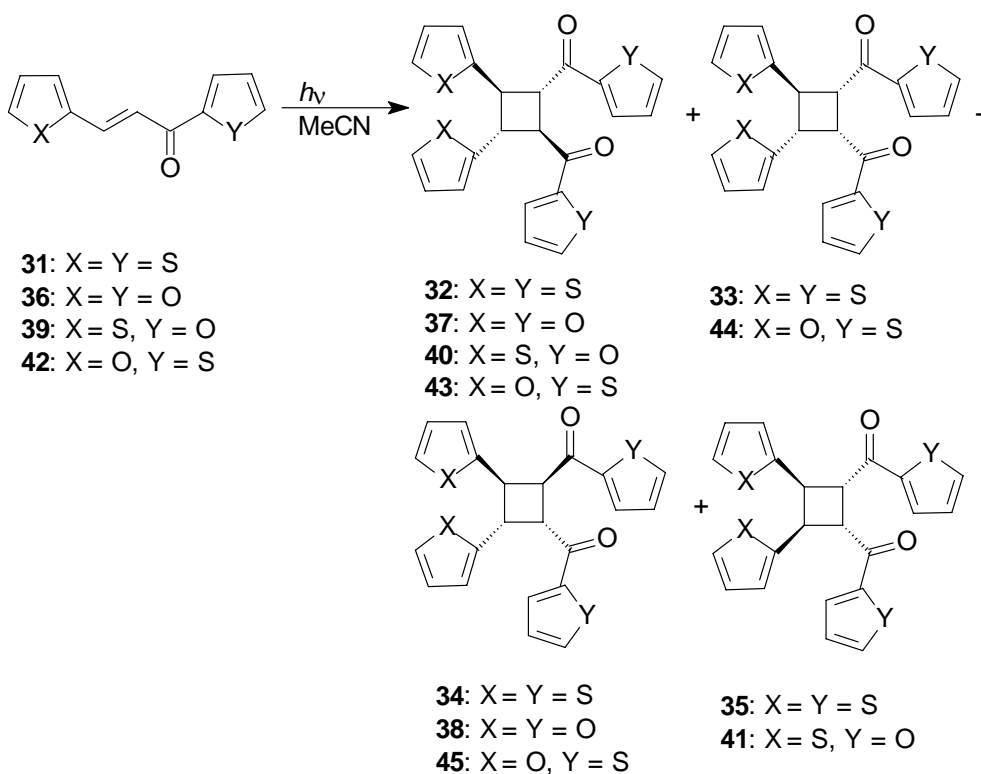
2.   Dimerization of alkenes bearing a carbonyl group

We tested the reactivity of both the acrylaldehyde derivative (**26**) and the methyl ketone (**28**). While the furylacrylaldehyde gave only the dimer (**27**) in 42% yield, the photoreaction of ketone (**28**) in the presence of benzophenone led to a 1:1 mixture of dimers (**29**) and (**30**) in 70% overall yield (Scheme 8).[19]

Scheme 8

Scheme 9

31: X = Y = S
36: X = Y = O
39: X = S, Y = O
42: X = O, Y = S

32: X = Y = S
37: X = Y = O
40: X = S, Y = O
43: X = O, Y = S

33: X = Y = S
44: X = O, Y = S

34: X = Y = S
38: X = Y = O
45: X = O, Y = S

35: X = Y = S
41: X = S, Y = O

The photochemical irradiation of 1,3-dithienyl-2-propen-1-one (**31**) in acetonitrile for 24 h gave a mixture of four products (Scheme 9).[25] It is noteworthy that in a previous paper the photochemical dimerization of **31** was described to occur only in 4% overall yield.[26] In our experiment we obtained the dimers in 62% yield.

If the reaction was carried out in the presence of benzophenone as triplet sensitizer, no significant change in the photochemical behavior of **31** was observed. The intersystem crossing quantum yield (Φ_{isc}) of **31** was 0.04 while the quantum yield of the reaction (Φ) was 0.1. All these data are in agreement with a mechanism involving the first excited singlet state. This hypothesis was tested by using PM3-RHF semiempirical method: the energy of both the HOMO and the LUMO of the S_0 of **31** is –9.42 eV and –1.23 eV, respectively. Furthermore, the energy of the LSOMO and the HSOMO of the excited singlet state of **31** is –8.00 eV and –4.17 eV, respectively. The best interaction between the above reported frontier orbitals could be obtained between the LSOMO-S_1 and the HOMO-S_0. However the LSOMO of the first excited singlet state is not a π orbital and it can not participate to frontier orbital control. The interaction between the HSOMO-S_1 and the LUMO-S_0 (Figure 3) is in agreement with the formation of head-to-head dimers.

The products obtained in the reaction of **31** can be rationalized by using the hypothesis that the reaction leads to the formation of the more stable isomers (Table 5).[19]

When the reaction was carried out on the furan derivative (**36**) we obtained a mixture of two products (**37**) and (**38**) with 38% overall yields (Scheme 9).
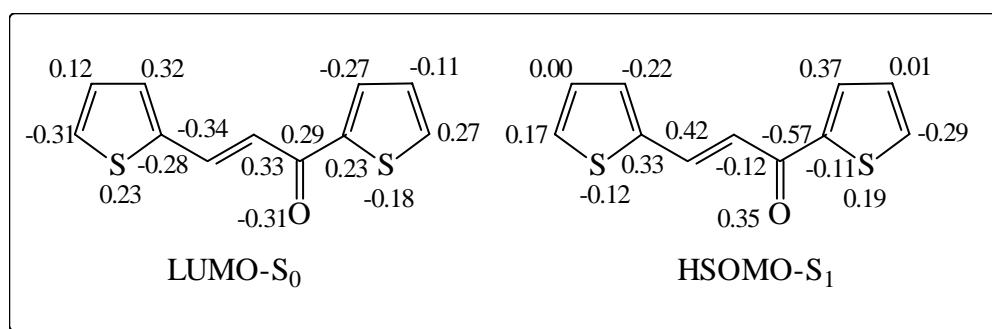

Figure 3 – Frontier orbitals of **31**.

When the irradiation was performed in the presence of benzophenone, **36** gave the same mixture of products in the same ratio. We assumed, then, that, also in this case, the reaction involves the photochemical behavior of the first excited singlet state. The energy of both the HOMO and the LUMO of the S_0 of **36** is –9.11 eV and –0.93 eV, respectively. The energy of LSOMO of S_1 is –7.88 eV, while that of HSOMO is –4.07 eV. Also in this case the best interaction would occur between the LSOMO of S_1 and the HOMO of S_0; however, the LSOMO is not a π orbital. The atomic coefficients of the HSOMO-S_1

and LUMO-S$_0$ are depicted in Figure 4. These data are in agreement with the formation of head-to-head dimers.

The heat of formation of all the possible head-to-head dimers accounts for the formation of the obtained products (Table 5).
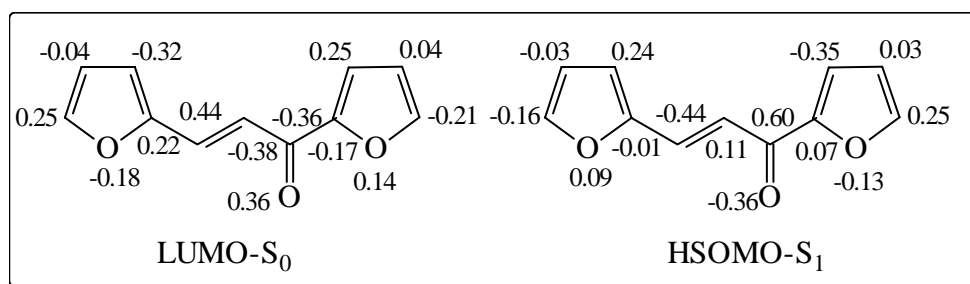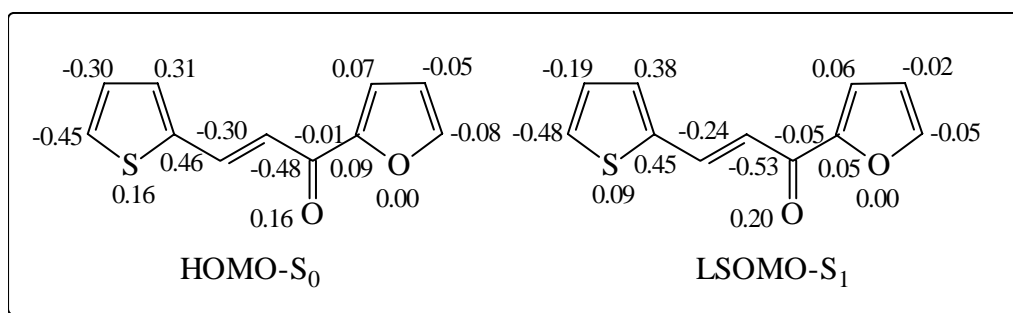

Figure 4 – Frontier orbitals of **36**.

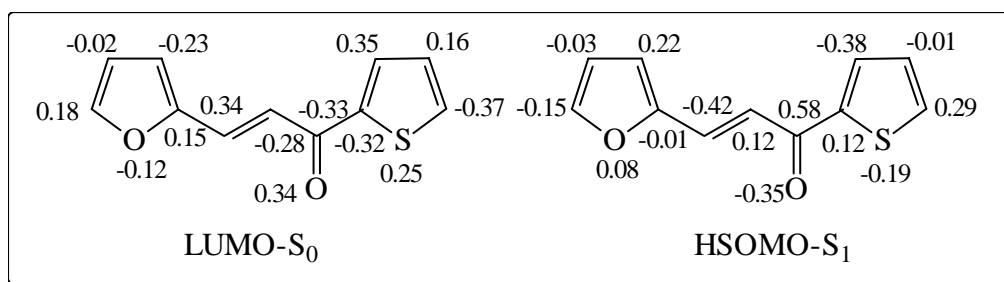**Figure 5** – Frontier orbitals of **39**.
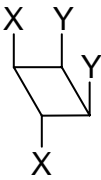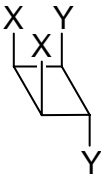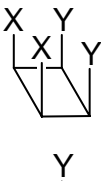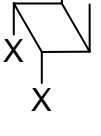
Figure 6 – Frontier orbitals of **42**.

In the case of **42** the energy of the HOMO-S$_0$ is –9.11 eV, while that of the LUMO is –1.11 eV; in the first excited singlet state the LSOMO and the HSOMO show the energy of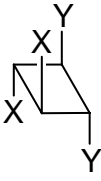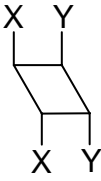 –7.96 eV and –4.14 eV, respectively. The best interaction would occur between the LSOMO-S$_1$ and the HOMO-S$_0$: however, the LSOMO is not a π orbital. The atomic coefficients of both the HSOMO-S$_1$ and the LUMO-S$_0$ are represented in Fig. 6, showing that, also in this case, only head-to-head dimers are allowed.

Table 5 – Heat of formation of dimers from chalcones

Dimer[a]	ΔH_f [kcal mol^{-1}]			
	From **31**	From **36**	From **39**	From **42**
	89	-56	17	15
	82	-63	9	11
	89	-57	22	15
	93	-55	22	17
	107	-46	35	27
	89	-56	16	16

a) For dimers obtained from **31**: X = 2-thienyl, Y = CO-(2-thienyl); for dimers obtained from **36**: X = 2-furyl, Y = CO-(2-furyl); for dimers obtained from **39**: X = 2-thienyl, Y = CO-(2-furyl); for dimers obtained from **42**: X = 2-furyl, Y = CO-(2-thienyl).

We carried out the photochemical dimerization also with compounds (**39**) and (**42**), which show both a thienyl and a furyl ring in the same molecule. The irradiation, without sensitizer, of **39** led to the formation of **40** and **41** with an overall yield of 57% (Scheme 9). Furthermore, the irradiation of compound (**42**) led to the formation of a mixture of three products (**43**, **44**, and **45**) with an overall yields of 79% (Scheme 9). Also in this case the reaction seems to involve the first

excited singlet state. In the case of **39**, the energy of the HOMO in the ground state is –9.34 eV, while the LUMO shows an energy of –1.15 eV; the first excited singlet state of **39** shows the LSOMO at –6.89 eV and the HSOMO at –3.75 eV. The best interaction could be obtained between HOMO-S_0 and LSOMO-S_1. These frontier orbitals are represented in Figure 5 and they show that only the formation of head-to-head dimers is allowed.

The analysis of the heat of formation of all possible head-to-head dimers are in agreement with the hypothesis that only the more stable isomers are obtained (Table 5).

3.   Dimerization in the presence of other electron withdrawing groups

The irradiation of **46** in the presence of benzophenone in acetonitrile gave a mixture of three cyclobutane derivatives (**47-49**) as described in Scheme 10.[27]

Scheme 10
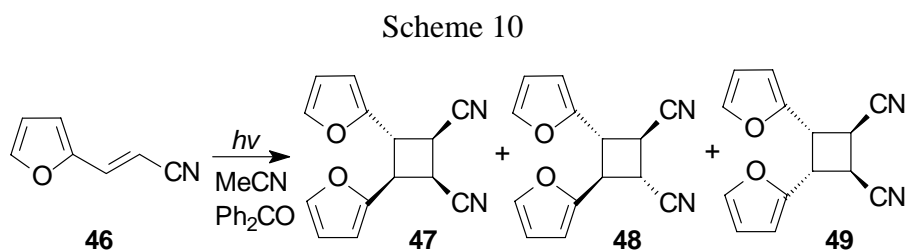
From a synthetic point of view it is noteworthy that the compound (**48**) obtained in the highest yield shows the same stereochemistry of some naturally occurring cyclobutanes isolated from Carribean sponges *Agelas sceptrum* and *Agelas conifera*.[28-30] The regiochemical behavior can be explained assuming frontier orbital control of the reaction. We estimated the HOMO and the LUMO energies for the compound (**46**) by using PM3 semiempirical method and the results are collected in Table 6. The best interaction occurs between the LSOMO of the excited triplet state and the HOMO of the ground singlet state. Nevertheless, the interaction between the HSOMO of the triplet state and the LUMO of the ground singlet state shows a very similar value. The L and HSOMOs for the triplet state and the HOMO and the LUMO for the ground singlet state of the same molecule are depicted in Figure 7.

Therefore, we can see that we have total superposition between both LSOMO/HOMO and HSOMO/LUMO of the reagents. These data are in agreement with the exclusive formation of head-to-head dimers. The stereochemical behavior of the dimerization of 3-(2-furyl)acrylonitrile can be explained calculating the heat of formation for all the possible head-to-head dimers. The data are collected in Table 7. We can see that the more stable dimers are the obtained ones in agreement with our previous reported

results. Furthermore, the different stability between the dimers accounts for the different yields observed. Nevertheless, it is noteworthy that the calculated differences between the dimers are very small. In particular, it is not clear why we obtained the compound (**49**) (heat of formation 76.74 kcal mol^{-1}) while we did not observe the formation of the dimer showing the heat of formation of 76.90 kcal mol^{-1}.

Table 6 - HOMO and LUMO of acrylonitrile derivatives

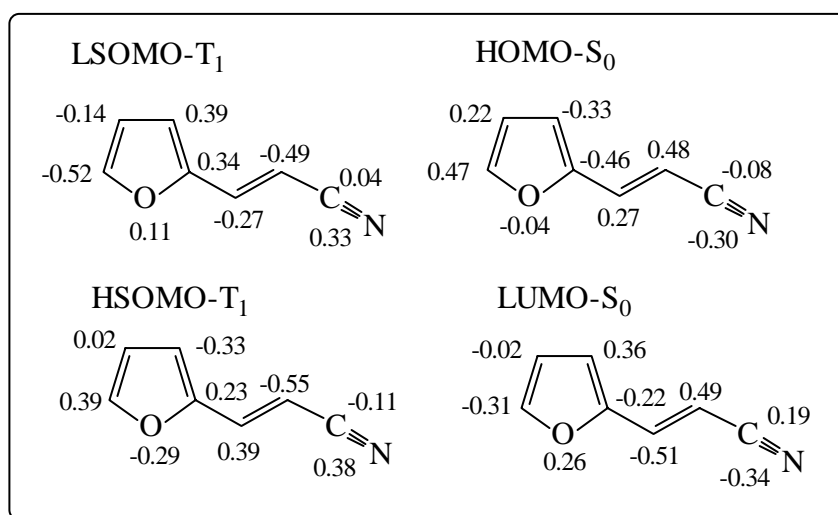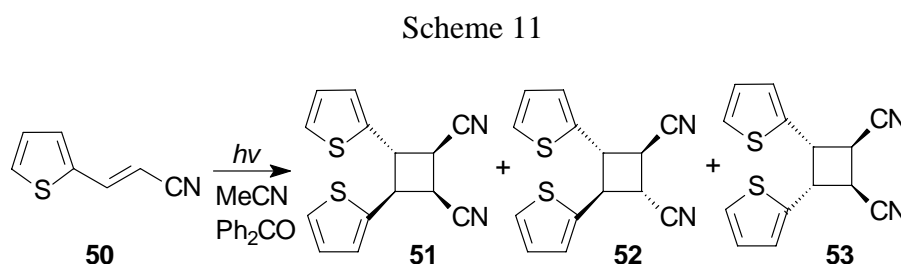| Compound	Electronic state	HOMO (eV)	LUMO (eV)	LSOMO (eV)	HSOMO (eV)
46	S_0	- 9.017	- 1.046		
	T_1		0.615	- 6.468	- 3.621
50	S_0	- 9.253	- 1.195		
	T_1		- 1.104	- 6.417	- 2.595

Figure 7 - LSOMO and HSOMO of T_1 and HOMO and LUMO of S_0 of compound (**46**).

When the photochemical reaction was performed on 3-(2-thienyl)acrylonitrile (**50**) (under the same conditions) we obtained the products described in Scheme 11.
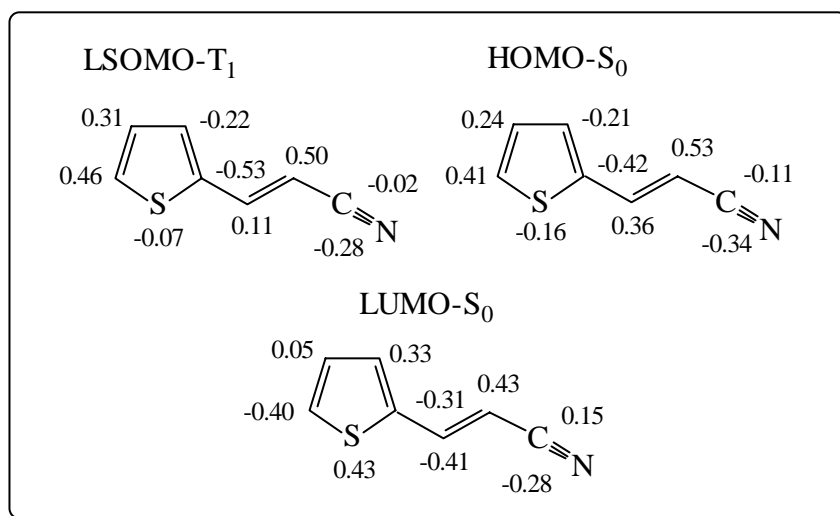
Scheme 11

Figure 8 - Frontier orbitals of compound (**50**).

Table 7 - Heat of formation of all the head-to-head dimers of arylacrylonitrile derivatives

Dimer	Heat of Formation (kcal mol^{-1})		Dimer	Heat of Formation (kcal mol^{-1})	
	Furan[a]	Thiophene[b]		Furan[a]	Thiophene[b]
	76.58	148.88		81.77	154.12
	73.31	146.48		85.67	161.82
	76.90	149.81		76.74	148.97

a) X = 2-Furyl, Y = CN; b) X = 2-Thienyl, Y = CN

We obtained the same type of products with similar yields. On the contrary, the conversion in this case was very low. In this case the regiochemistry can be explained considering the interactions between both the LSOMO of the triplet state of **50** and the HOMO of the fundamental singlet state of the same molecule and the HSOMO of the triplet state and the LUMO of the fundamental singlet state (Table 6, Figure 8). The best interaction was obtained between the HSOMO of T_1 and LUMO of S_0. However, the HSOMO is not a π orbital and it can not give frontier orbital control.

It is noteworthy that, assuming that the only frontier orbital interaction is that between the HSOMO of T_1 and the LUMO of S_0, in this case the gap between these two orbitals is higher than that obtained using compound (**46**). This datum is in agreement with the observed lower reactivity of **50** in comparison with **46**.

Also in this case, the formation of compounds (**51-53**) can be explained on the basis of the different stability of all the possible dimers, as reported in Table 7.

We tested also the sensitized photochemical dimerization of 1,1-dicyano derivatives (**54a-b**) (Scheme 12).[25] The irradiation of **54a** in the presence of benzophenone gave the dimer (**55a**) in 3.4% yield. The compound (**54b**) did not react in the presence of benzophenone, while, when acetophenone was used as sensitizer, the formation of a dimer was observed in very low yield (1.5%).
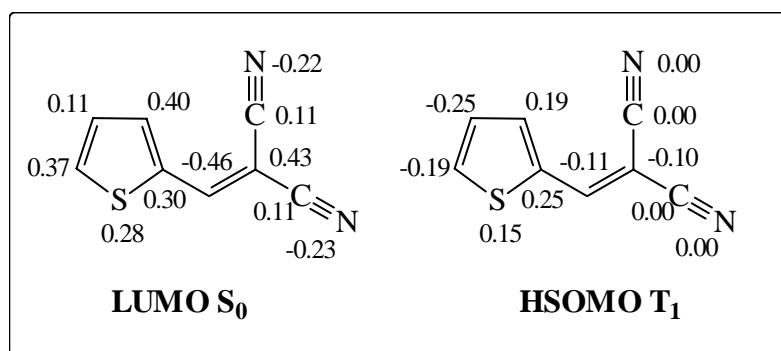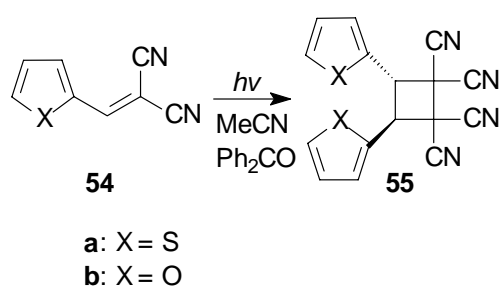
Scheme 12

a: X = S
b: X = O

Figure 9 – Frontier orbitals of **54a**

The HOMO of **54a** was at –9.79 eV while the LUMO was at –1.82 eV. The triplet state of **54a** showed the LSOMO at –6.40 eV and the HSOMO at –2.87 eV. The best interaction can be obtained between the LUMO-S_0 and the HSOMO-T_1: these frontier orbitals are depicted in Figure 9 and they do not allow a good superposition. This result is in agreement with the observed low reactivity of the substrate.

We tested also the photochemical reactivity of 2-(2-heteroaryl)nitroethene derivatives. These compounds were irradiated in acetonitrile in the presence of benzophenone as triplet sensitizer. The results are summarized in Scheme 13.

Scheme 13
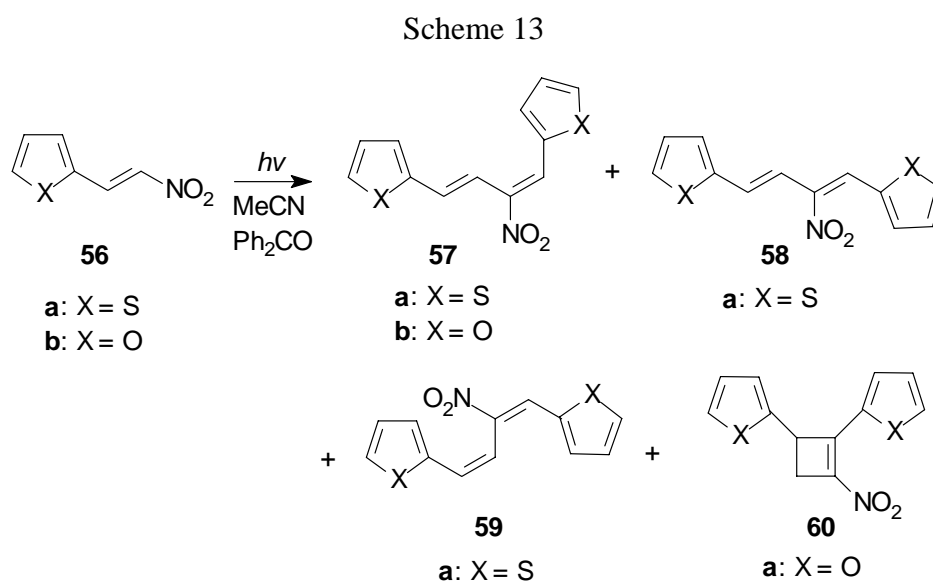
The irradiation of the thienyl derivative (**56a**) did not give the formation of the expected dimers but gave a mixture of three products where **57a** was the main product. These compounds are dimers of the substrate with the loss of HNO_2. The same behavior was observed in the case of the furan derivative (**56b**). In this case we observe the formation of two products where **57b** is analogue to that obtained with **56a** and a cyclobutene derivative (**60a**), probably deriving from a photochemical reaction on a dimer of the type (**57-59**).
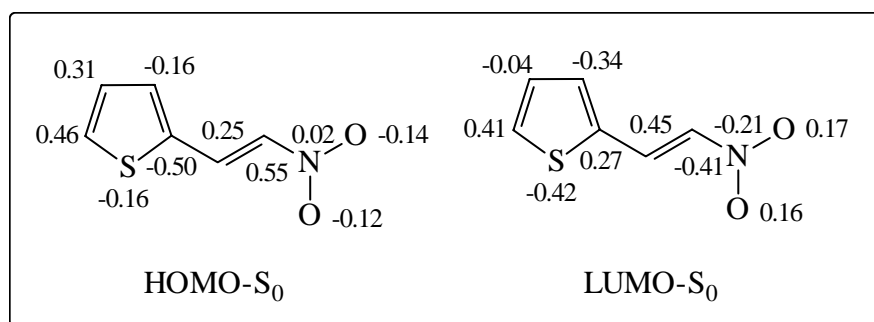

Figure 10 – Frontier orbitals of S_0 state of **56a**

The HOMO of the ground singlet state of **56a** is shown in Figure 10 and it was at –10.09 eV. The LUMO of the S_0 state was at –1.75 eV (Figure 10). The LSOMO of the lowest excited triplet state was at –6.58 eV while the HSOMO was at –3.00 eV (Figure 11). The best interaction between the frontier orbitals can be obtained between HSOMO-T_1 and LUMO-S_0. We can note total superposition of the frontier orbital involved.
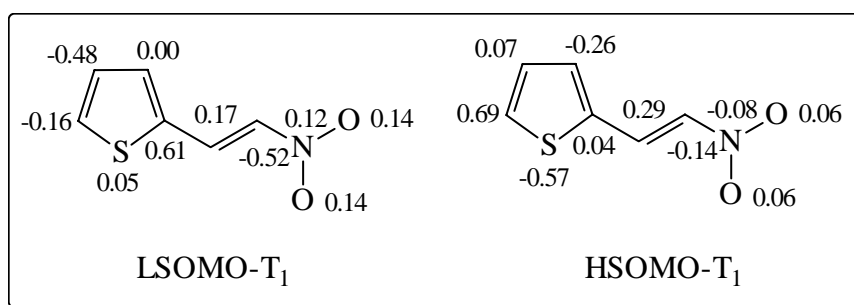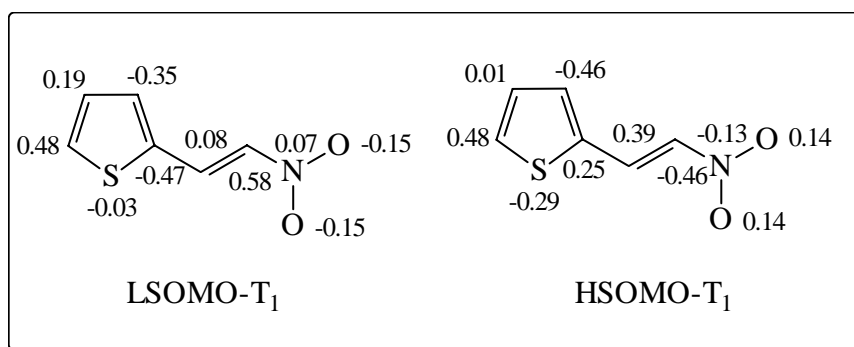

Figure 11 – Frontier orbitals of T_1 state of **56a**

Figure 12 – Frontier orbitals of S_0 state of **56b**
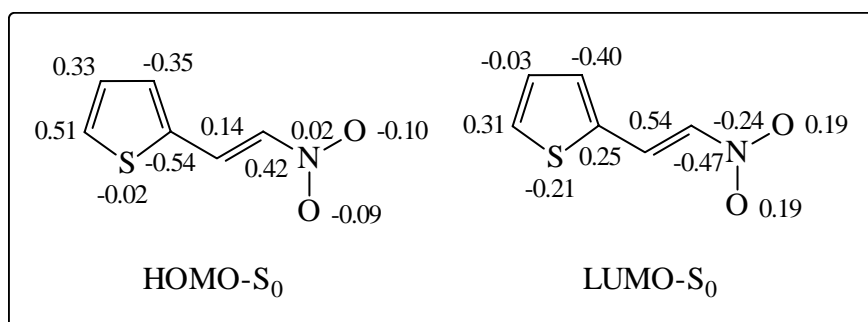
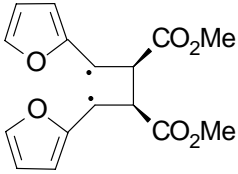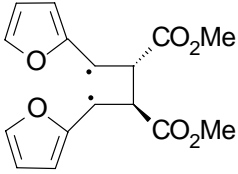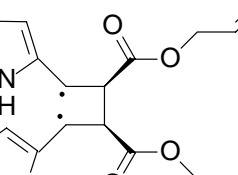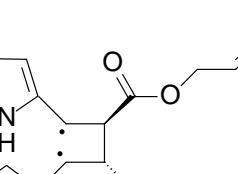**Figure 13** – Frontier orbitals of T_1 state of **56b**

The HOMO of the ground state of **56b** was at –9.78 eV and the LUMO was at –1.52 eV (Figure 12). The LSOMO and the HSOMO of the lowest excited triplet state of the same molecule was at –6.94 eV and –

4.54 eV, respectively (Figure 13). The best interaction can be obtained between the HOMO-S_0 and the LSOMO-T_1.

The data can explain the observed behavior of **56a** and **56b**. The superposition of the frontier orbitals is allowed and the reaction, as in the case of **56a**, we obtained reasonable yields of the products. We do not obtain cyclobutanes, but probably this behavior depends on the fate of the biradical intermediate deriving from the coupling between the triplet state of the substrate and the ground state of the same molecule.

Table 8 - ΔH_f of selected intermediates

Compound	ΔH_f [kcal mol^{-1}]
	-121
	-120
	-10
	-12

4.   Conclusion

The photochemical dimerization of alkenes bearing both pentaatomic aromatic heterocyclic rings and electron withdrawing groups can be understood assuming frontier orbital control of the reaction. This control determines the regiochemical behavior of the dimerization (head-to-head versus head-to-tail products).

The reaction can occur in the first excited singlet state as in the case of the compounds (**31**, **36**, **39**, and **42**). Using these substrates the reaction is concerted, giving the product without the presence of the singlet biradical intermediate. In the other cases the reaction occurs through the first excited triplet state. The reaction leads to the formation of the corresponding triplet biradicals. The coupling of the carbons bearing the electron withdrawing groups determines the stereochemistry of two carbons in the cyclobutane. We verified if this approach is in agreement with the experimental results. We calculated the ΔH_f of the biradical intermediates in the case of methyl 3-(2-furyl)acrylate (**12**) and in the case of allyl urocanate (**24**). Using **12** we obtained two cyclobutanes with both Z and E relationship between the ester functions. The product showing Z stereochemistry was favored. In the case of compound (**24**) the only product obtained showed a E relationship between the ester functions. The results of our calculations is reported in Table 8.

We can see that, in the case of methyl furylacrylate the *syn* dibiradical is favored in agreement with experimental results. $\Delta\Delta H_f$ between the isomers is 1 kcal mol^{-1}. Probably this value allows the formation of both the isomers. In the case of allyl urocanate the *anti* isomer is favored. Furthermore, $\Delta\Delta H_f$ is 2 kcal mol^{-1}: this difference probably accounts for the selective formation of a cyclobutane showing a E relationship between the ester functions.

The evolution of the biradicals obtained through the coupling of the carbons bearing the electron withdrawing groups can be understood considering the stability of the cyclobutane rings. In fact, all the reactions tested showed that only the more stable cyclobutanes were obtained.

In conclusion we have shown that the photochemical dimerization in solution of the heterocyclic substituted alkenes bearing electron withdrawing groups can be predicted on the basis of this photophysical and chemical properties.

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