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Photochemical Reactivity of Aromatic and Heteroaromatic Nitroderivatives in the Presence of Arylalkenes

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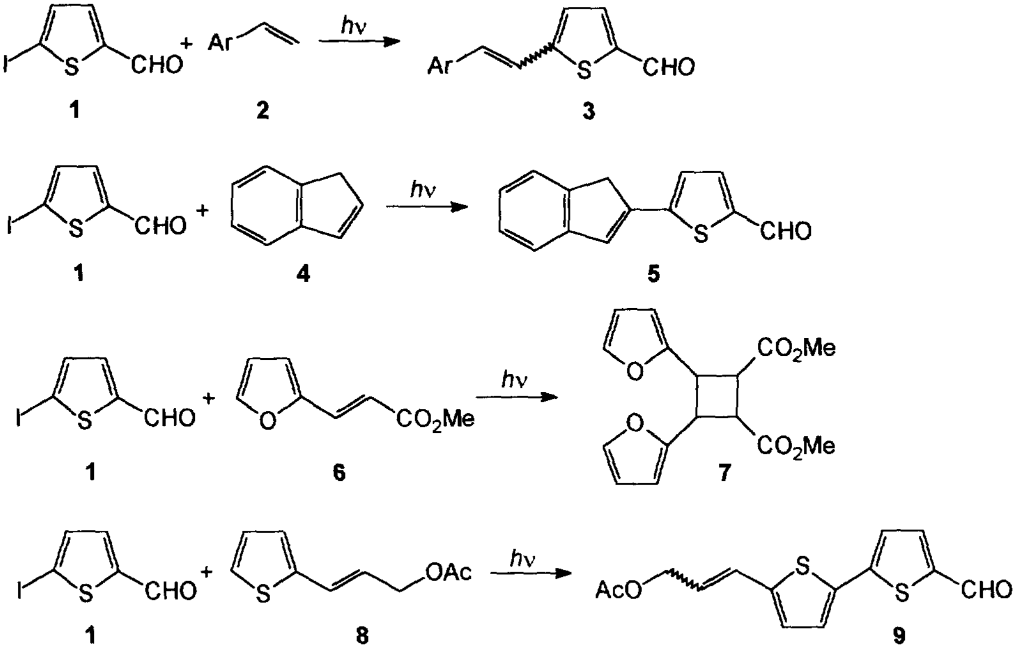
Abstract: The irradiation of styrene in the presence of nitroarenes in acetonitrile gives the corresponding nitrones in high yields. However, when 4-methyl-5-ethenylthiazole is used as arylalkene the starting material is converted to a pyrrole analogous of thianthrene. On the contrary, when 1,1-diphenylethylene is used, the main product observed is benzophenone. Nitrones are obtained only as minor products. An unusual coupling product, where a substitution reaction has occurred on the carbon bearing the nitro group, is also obtained. *trans*-Stilbene is unreactive under the same photochemical conditions, and it gives in low yields only benzaldehyde. Finally, indene gives, when aromatic nitro derivatives are used, only oxidation products, while, when heteroaromatic nitro derivatives are used, only substitution products on the nitro group are observed. The above described reactivity can be explained by using the results of AM1 semiempirical calculations on the frontier orbitals of the reagents. Both the nature of the LSOMO of the nitroarenes and the dipole moments of the reagents can account for the observed reactivity. The nitrone obtained in the photochemical reaction between styrene and nitrobenzene is used as starting material in a 1,3-dipolar cycloaddition reaction with styrene. Copyright © 1996 Elsevier Science Ltd

Some years ago we reported that 5-iodothiophene-2-carbaldehyde (**1**) reacted with arylalkenes (**2**) to give the correspoding coupling products (Scheme 1).[1] In this case we observed the formation of the product derived from the attack of the haloheterocyclic derivatives on the alkene to give a *cis-trans* mixture of **3**. While the reaction did not show the same selectivity when a methyl group is present on the molecule in α position on the alkene,[2] this type of reaction worked very well when the substrate had an alkyl group in the β position on the alkene to give **5** (Scheme 1).[3] However, if an electron-withdrawing group was present on the molecule, such as in **6**, the expected photocoupling reaction did not occur and the dimerization of the starting material was detected.[4-6] On the contrary, if a weak electron-withdrawing group was present on the substrate, the photocoupling reaction did occur. However, while using 2-ethenylthiophene as substrate, the photocoupling reaction occurred on the alkene, in this case only the coupling on the thiophene ring was observed (Scheme 1).[7,8]

Scheme 1



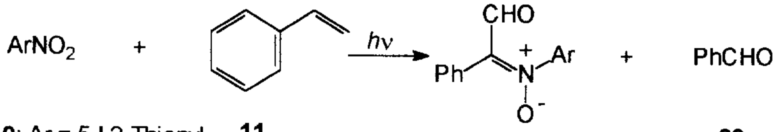
On the basis of this previous work, we decided to study the photochemical reactions of 2-iodo-5-nitrothiophene with arylalkenes after a preliminary study on the reactivity of the same substrate with aromatic and heteroaromatic compounds.[8,9] Considering our previous results we looked for the coupling products between the carbon bearing the halogen substituent on the substrate and the arylalkenes, and, in this case, we wanted to verify the regiochemistry of this reaction.[10]

Results and Discussion

2-Iodo-5-nitrothiophene (**10**) can be easily obtained by nitration of 2-iodothiophene.[11] It showed a strong absorption in the UV spectrum at 341 nm (log ε 4.05) and it did not show any fluorescence signal. The irradiation of **10** with styrene (**11**) in acetonitrile for 2 h with a high-pressure mercury arc in the presence of a Pyrex filter gave a 2:1 mixture of the coupling products **12** and **13**, surprisingly (Scheme 2, Table 1).[12]

In this case we observed that a coupling reaction occurred but the reaction involved the participation of the nitro group while the halogen atom did not participate in the reaction. In fact, **13** probably derived from **12** through a homolytic fission of the C-I bond and this homolytic fission did not have a role in the promotion of the reaction. To test this statement the same reaction was performed on 2-nitrothiophene (**14**). 2-Nitrothiophene showed two absorptions in the UV spectrum at 280 and 309 nm, respectively. The irradiation of **14** in the presence of styrene gave **13** in good yields (Scheme 2, Table 1). The same trend was observed when using 2-nitrofuran (**15**) as the starting material. In all the experiments we obtained high yields of the corresponding nitrone **16** (Scheme 2, Table 1).

Scheme 2



10: Ar = 5-I-2-Thienyl **11**
14: Ar = 2-Thienyl
15: Ar = 2-Furyl
17: Ar = Phenyl
19: Ar = *p*-Tolyl

12: Ar = 5-I-2-Thienyl
13: Ar = 2-Thienyl
16: Ar = 2-Furyl
18: Ar = Phenyl
21: Ar = *p*-Tolyl

20

Table 1 - Photochemical Reaction of Nitroarenes with Styrene

Substrate	Irradiation Time (h)	Product	Yields (%)[a]
10	2	**12**	55
		13	27
14	2	**13**	78
15	3	**16**	80
17	2	**18**	73
19	2	**21**	9

a) All the yields refer to isolated chromatographically pure compounds.

Finally, we found that this reaction is not restricted to heteroaromatic nitro derivatives. Nitrobenzene showed an absorption in the uv spectrum at 330 nm. Also the irradiation of this compound in the presence of styrene gave the nitrone **18** (Scheme 2, Table 1). The absorption of nitrobenzene at 330 nm has been assigned both to a $n \rightarrow \pi^*$ transition or to a $\pi \rightarrow \pi^*$ transition.[13-15] Our calculation by using AM1 semiempirical method showed that the first excited triplet state in nitrobenzene is a n,π^* excited state while 2-nitrothiophene showed a π,π^* triplet state. In Figure 1 we represent the lowest SOMOs for nitrobenzene and 2-nitrothiophene. The above reported difference in the reactive excited state does not influence the reactivity of the substrate in the reaction with styrene.

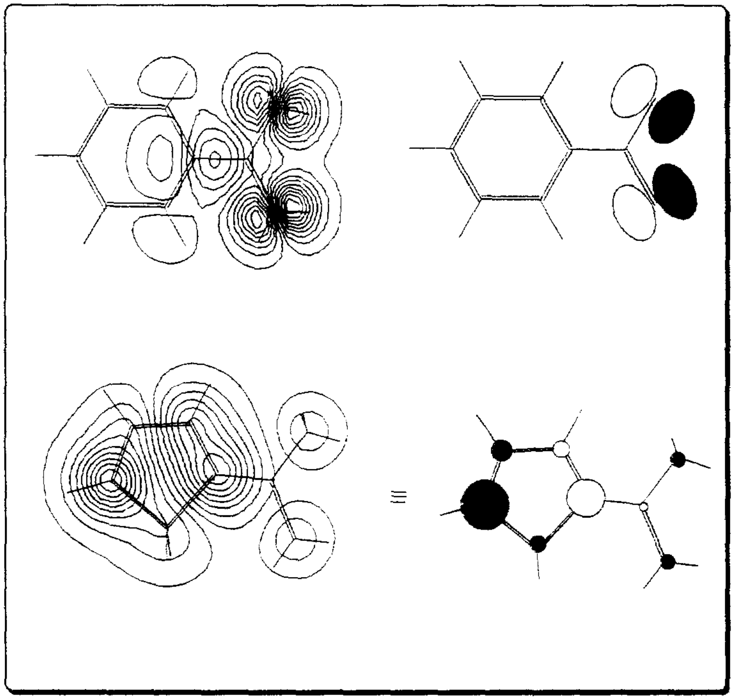
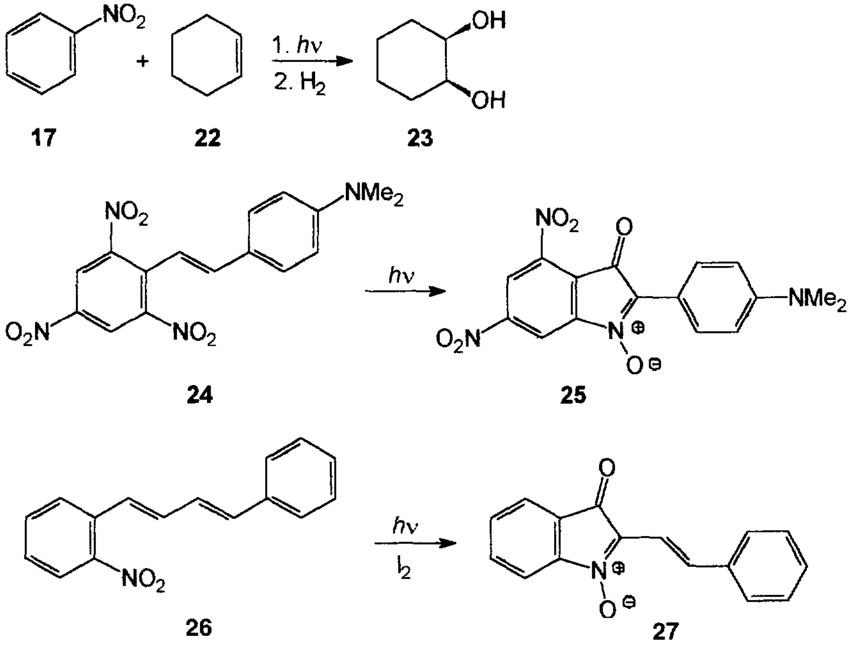


Figure 1 - Lowest SOMO of nitrobenzene and 2-nitrothiophene

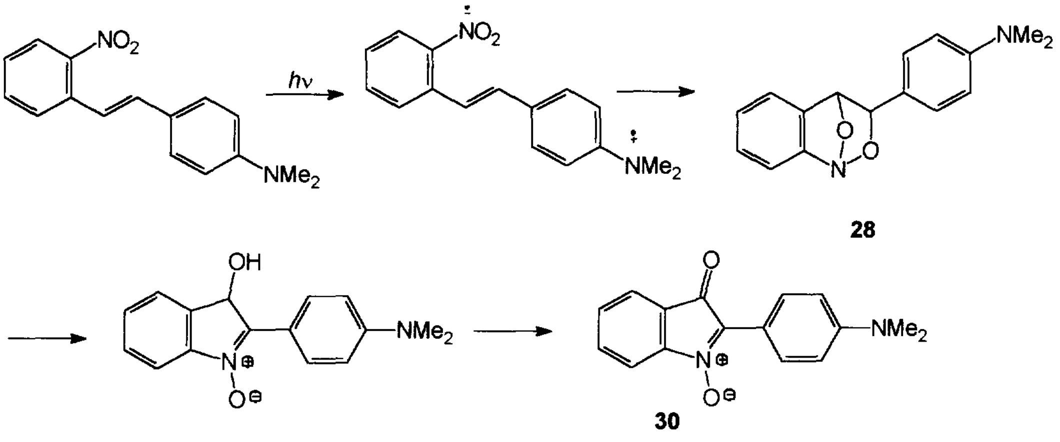
Scheme 3



Only when *p*-nitrotoluene was used as substrate did we observe a very different behaviour. In this case, the main reaction product was benzaldehyde (86%) while the nitrone **21** was obtained in 9% yield only.

The reaction depicted in Scheme 2 can be rationalized assuming an addition reaction of the nitro derivatives on the alkene. The photochemistry of nitroarenes in the presence of alkenes has been investigated. The addition of nitrobenzene (**17**) to the alkene **22** gives the corresponding 1,2-diols (**23**) after hydrogenation (Scheme 3).[16-18] Photochemical reaction of the nitrostilbene **24** gives the compound **25** while the extension of this reaction to the nitro derivative **26** gives compound **27** (Scheme 3).[19,20] The conversion **24** → **25** occurs in 3-44% yields depending on the substituents on the stilbene and the conversion **26** → **27** occurs in 9-30% yields. Therefore, we can see that the intermolecular conversion described in the Scheme 2 has been described in the intramolecular form reported in the conversion **24** → **25**. Nevertheless, the yields of the intramolecular process are poor. For the conversion **25** → **25** the authors propose a mechanism involving an intramolecular electron transfer followed by the addition of the nitro group to the alkene to give the intermediate **28**. The transposition of **28** to give **29** and the subsequent oxidation account for the formation of the nitrones (Scheme 4).[19]

Scheme 4



28

29

30

Splitter and Calvin reported spectroscopic evidences for the formation of **29**. They detected the UV spectrum of this intermediate. Compound **29** was stable as shown by the concentrations present in the reaction mixture after the irradiation. The conversion **29** → **30** was proposed to be a reaction occurring in the dark. Our results are in agreement with this mechanistic hypothesis, but not with a slow final oxidation step. We were unable to detect the formation of an intemediate which implies that the final oxidation is not as slow as in the intramolecular reaction.

The hypothesis reported in Scheme 4 implies that the first step of the reaction is an electron transfer process. We can estimate the efficiency of this electron transfer process by using the Weller equation (*1*), where

$E_{½}^{Ox}(D)$ and $E_{½}^{Red}(A)$ are the oxidation potential of the donor and the reduction potential of the acceptor, respectively; ΔE_{exc} the excitation energy, F = 96490 C, e = 1.602 x 10^{-19} C, ε_0 = 8.854 x 10^{-12} Fm^{-1}, ε is the dielectric constant of the solvent and a is the encounter distance (7 A).[21-33]

$$\Delta G = F\left[E_{½}^{Ox}(D) - E_{½}^{Red}(A)\right] - \Delta E_{exc} + \frac{e^2 N}{4\pi\varepsilon_0 a}\left(\frac{1}{\varepsilon} - \frac{2}{37.5}\right) \qquad (1)$$

For nitrobenzene $\left[E_{½}^{Ox}(D) + \Delta E_{exc}\right]$ is 1.4 V while for styrene $E_{½}^{Red}(A)$ is 1.90 V *vs* SCE.[34,35] In this case the Weller equation gave ΔG = - 0.56 eV in agreement with an electron transfer process.

On the basis of these results we tested the photochemical reactivity of the nitroarenes with other arylalkenes. We wanted to test the photochemical reactivity of nitroarenes with heteroarylalkenes. In fact, studying the reactivity of 5-iodothiophene-2-carbaldehyde with arylalkenes, we found that heteroarylalkenes showed the same trend of reactivity allowing us to obtain interesting products.[1] 2-Vinylthiophene can be obtained from thiophene by reaction with acetaldehyde and subsequent elimination.[36,37] 2-Vinylfuran can be obtained through decarbonylation of 3-(2-furyl)acrylic acid.[38] Unfortunately, these compounds are not stable and we selected 4-methyl-5-ethenylthiazole as a substrate for our photochemical reactions.

In order to perform this type of reaction we estimated the capability of this substrate to give electron transfer reactions in the presence of nitroarenes. 4-Methyl-5-ethenylthiazole showed an anodic signal in acetonitrile with sodium perchlorate as supporting electrolyte with peak potential *vs* the adopted reference electrode of 1.78 V. Cyclic voltammetric experiments showed that this compound yields an irreversible electrode process: no cathodic peak is present. Usually, reversible oxidation potentials should be used in the Weller equation. However, the use of irreversible oxidation potentials has been reported.[39-42] On the basis of these data we can calculate ΔG value for the electron transfer process. For this purpose we corrected the obtained potential *vs* Ag^+/Ag. Furthermore, the correction of peak potential as reported by Miller was considered.[43] This way, we obtained ΔG = 0.05 eV for the electron transfer process.

4-Methyl-5-ethenylthiazole showed absorptions at 275 (log ε 3.9) and 224 nm (log ε 3.6). 2-Nitrothiophene, 2-nitrofuran and nitrobenzene showed absorptions at wavelengths longer than 300 nm [309 (log ε 3.8), 315 (log ε 3.9), and 330 nm (log ε 2.1), respectively]. In our experiments we used a Pyrex filter that cuts off wavelengths lower than 300 nm.

The irradiation of 4-methyl-5-ethenylthiazole in the presence of nitroarenes in acetonitrile was carried out in an immersion apparatus for 72 h. Column chromatography of the crude product gave moderate yields of the compound **32** (Scheme 5, Table 2). We obtained the same product by changing the nitroarene. The product of the photochemical reaction was identified on the basis of its spectroscopic properties. ^{1}H-NMR spectrum showed a singlet at δ 10.8 ppm (aldehydic proton), a singlet at δ 8.95 ppm, identified as a proton on nitrogen in an aromatic compound such as pyrrole,[44] and a singlet at δ 2.74 ppm consistent with a methyl group on an alkene. ^{13}C-NMR spectrum showed a signal at δ 182.1 ppm in agreement with the presence of an aldehyde, signals at δ 161.6 and 158.5 ppm which can be assigned to aromatic carbons substituted with electron donating groups, two other signals of aromatic carbons at δ 132.7 and 128.9 ppm and, finally, a signal at δ 16.0 ppm identified as a methyl group. The mass spectrum showed a peak at *m/z* 278 corresponding to the molecular ion. A fragmentation peak was observed at m/z 246, that can be obtained from M^+ with a loss of sulfur. This type of fragmentation is common in thianthrene. All these data are in agreement with the proposed structure.

Scheme 5

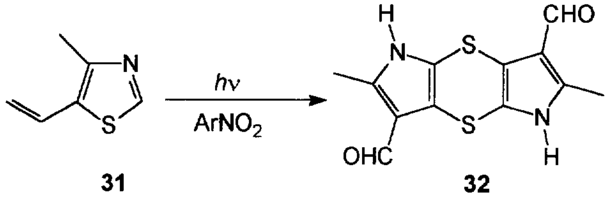


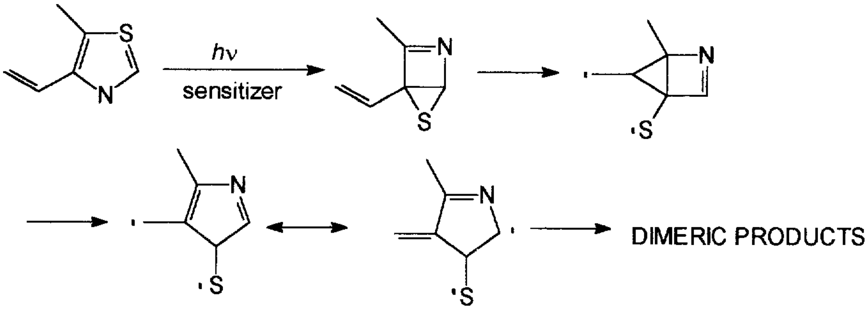
Table 2 - Photochemical Behaviour of 4-Methyl-5-ethenyl thiazole

Nitroarene	Irradiation time (h)	Yields (%)[a]
Nitrobenzene	72	30
4-Nitrotoluene	72	29
2-Nitrothiophene	72	26
2-Nitrofuran	48	27

a) All the yields refer to isolated chromatographically pure products

In this case we do not observe an electron transfer process in agreement with the calculated ΔG value.

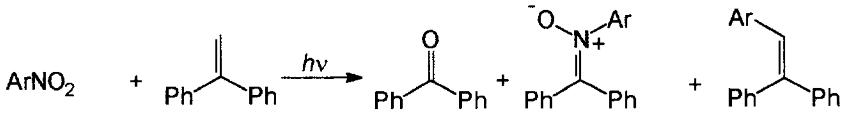
Scheme 6



The observed reactivity can be explained on the basis of an energy transfer process able to give the excited triplet thiazole. Excited thiazole can give an isomerization reaction.[45-51] In this case the direct participation of the vinyl group can account for the formation of the dimeric product (Scheme 6). There are some unsolved aspects in this reaction and we hope they will be the object of work in the near future.

In order to screen other arylalkenes we tested the reactivity of 1,1-diphenylethylene. In this case the irradiation in the presence of nitrobenzene gave a mixture of two compounds (Scheme 7, Table 3).

Scheme 7



17: Ar = Phenyl **33** **34** **35**: Ar = Phenyl **38**: Ar = 4-I-Phenyl

36: Ar = 4-I-Phenyl **37**: Ar = 4-I-Phenyl **39**: Ar = 5-Nitro-2-thienyl

10: Ar = 5-I-2-Thienyl **40**: Ar = 5-I-2-Thienyl

14: Ar = 2-Thienyl **41**: Ar = 2-Thienyl

Table 3 - Photochemical reactions of nitroarenes with 1,1-diphenylethylene

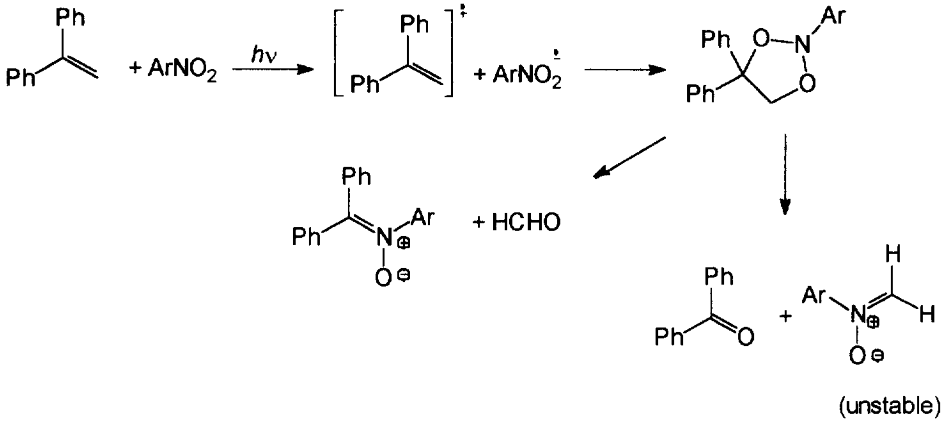
Nitroarene	Irradiation time (h)	Conversion (%)	Product	Yields (%)[a]
Nitrobenzene	5.33	58	**34**	63
			35	32
p-iodonitrobenzene	4	50	**34**	68
			37	10
			38	22
2-iodo5-nitrothiophene	2	100	**34**	68
			39	19
			40	9
2-nitrothiophene	2	100	**34**	88
			41	10

a) All the yields refer to isolated chromatographically pure compounds

The nitrone **35** was obtained in 32% yields while the main product of the reaction was benzophenone. This latter compound was the main product in all the reactions attempted with this substrate. Thus, where *p*-iodonitrobenzene (**36**) was used as substrate the nitrone **37** was obtained only in low yields (Scheme 7, Table 3). It is noteworthy that, in this case, we observed the formation of a new product, compound **38**, where the coupling between 1,1-diphenylethylene and the nitroarene has been performed through the substitution of the nitro group (Scheme 7, Table 3). The same trend was observed when 2-iodo-5-nitrothiophene was used as substrate. With the main product (benzophenone) we observed small quantities of both the substitution product on the carbon bearing the nitro group (Scheme 7, Table 3). Finally, when 2-nitrothiophene was irradiated in the presence of 1,1-diphenylethylene, with benzophenone the substitution product on the carbon bearing the nitro group was observed (Scheme 7, Table 3). In conclusion. by using as arylalkene 1,1-diphenylethylene, we can see that 1. the nitroarenes were less reactive than nitroheteroarenes (Table 3), 2. the main product of the reaction was benzophenone, and 3. some substrates gave an unusual product derived from a substitution reaction on the nitro group.

The formation of benzophenone can be explained considering the mechanism reported in Scheme 8. In this case the addition product derived from the attack of the nitro group on the alkene cannot give the nitrone derivative. The transposition reaction described in the Scheme 4, in this case, can give only fission products where the main product is benzophenone, while the minor products are the nitrones **35** and **37** (Scheme 8).

Scheme 8



Furthermore, we obtained as minor product, in some cases, products deriving from a substitution reaction on the carbon bearing the nitro group. Nucleophilic photosubstitution reactions where the nitro group is the leaving group is not a very common reaction. Thus, *p*-nitroanisole gave the pyridinium derivative if irradiated in pyridine, or 1,3,5-trinitrobenzene gave 3,5-dinitrophenol if irradiated in the presence of NaOH.[52-55] Here we want to note that there are no examples in the literature about a photosubstitution reaction on a nitro group where the nucleophile is an alkene.

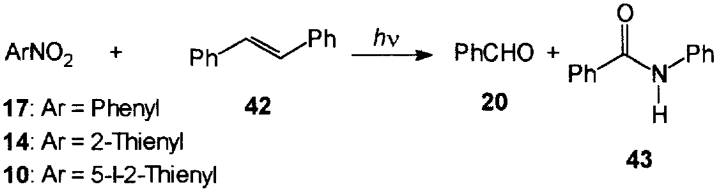
After 1,1-diphenylethylene we used the isomeric compound *trans*-stilbene. *trans*-Stilbene showed $E^{Red}_{1/2}(A) = 1.5$ V,[34] and, then, for the reaction with nitrobenzene, we obtained from equation (*1*) $\Delta G = 0.04$ eV. This compound showed, in agreement with this datum, a small reactivity (Table 4). After a prolonged reaction time only 16% of nitrobenzene reacted, showing that this reaction gave benzaldehyde and the amide **43** (Scheme 9, Table 4). On the contrary, when nitroheterocyclic derivatives were used as substrates, only benzaldehyde was obtained after prolonged irradiation times (Scheme 9, Table 4).

Table 4 - Photochemical reactions of nitroarenes with *trans*-stilbene

Nitroarene	Irradiation time (h)	Conversion (%)	Product	Yields (%)[a]
Nitrobenzene	24	16	**20**	78
			43	22
2-Nitrothiophene	24	25	**20**	100
2-Iodo-5-nitrothiophene	25	34	**20**	100

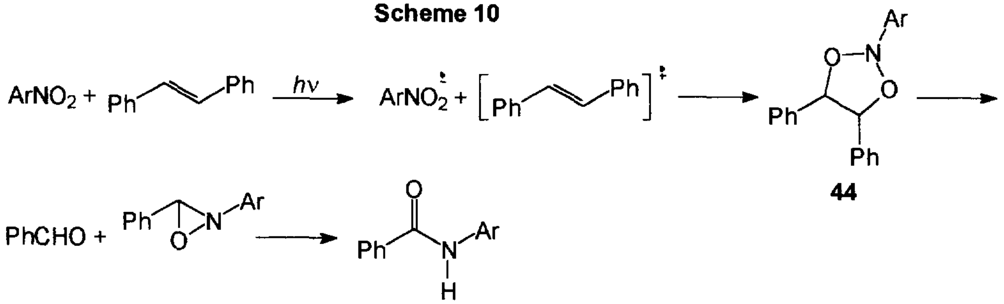
a) All the yields refer to isolated chromatographically pure compounds

Scheme 9



Also in this case the reactivity of the substrate can be understood on the basis of the above reported scheme. In fact, the reaction can evolve through the formation of a cyclic adduct between *trans*-stilbene and the nitro derivatives (Scheme 10). However, while in the previous reported reactions (Scheme 8) the fragments deriving from the decomposition of this adduct could be unstable nitrones, in this case the fragmentation of the adduct **44** can give stable compounds (benzaldehyde and the amide).

Scheme 10



Finally, we tested as reagent the arylalkene indene. In this case $E_{1/2}^{Red}(A)$ was reported to be 1.2 V.[34] Then, the Weller equation gave for the reaction with nitrobenzene $\Delta G = -0.26$ eV and, on the basis of this value, we anticipated a good reactivity of this substrate in the reaction with nitroarenes. When indene was irradiated in the presence of nitrobenzene, the main product obtained was *o*-tolylglyoxal (**45**) (Scheme 11, Table 5). The same trend was observed when *p*-iodonitrobenzene was used as starting material. However, in this case we obtained comparable yields of 2-indanone (**46**) (Scheme 11, Table 5).

Scheme 11

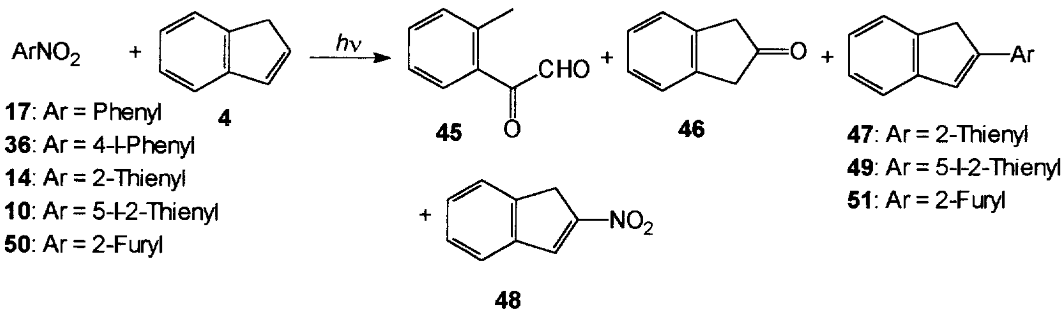


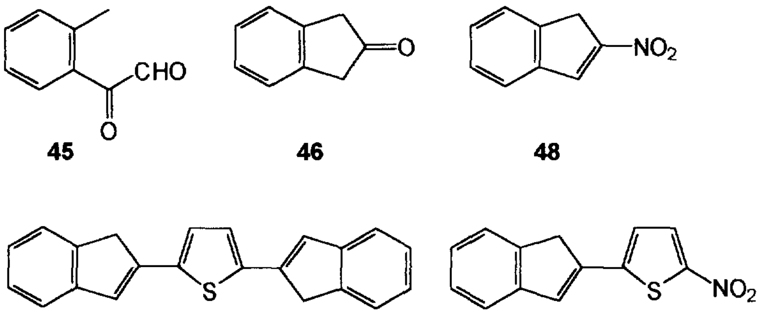
Table 5 - Photochemical reaction of nitroarenes with indene

Nitroarene	Irradiation time (h)	Conversion (%)	Product	Yields (%)[a]
Nitrobenzene	24	82	**45**	85
			46	9
p-Iodonitrobenzene	18	40	**45**	40
			46	50
2-Nitrothiophene	1	100	**45**	6
			46	8
			47	66
			48	20
2-Iodo-5-nitrothiophene	1	100	**47**	25
			49	75
2-Nitrofuran	1	100	**48**	23
			51	52

a) All the yields refer to isolated chromatographically pure compounds.

Using 2-nitrothiophene as reagent we observed a completely different behaviour. In fact, the irradiation of **14** in the presence of indene for 1 h gave good yields of the substitution product **47** (Scheme 11, Table 5). In this case we observed the formation of some by-products. We obtained low yields of 2-indanone and of the aldehyde **45**. Furthermore, 2-nitroindene (**48**) was obtained in low yields (Scheme 11, Table 5). The use of 2-iodo-5-nitrothiophene as starting material gave a very similar reaction mixture. In this case, high yields of the substitution product **49** were obtained (Scheme 11, Table 5). Also in this case we obtained as minor product the dehalogenated compound **47**. GC-MS analysis of the crude reaction mixture showed the formation of traces of some other compounds whose structures are reported in Scheme 12. When 2-nitrofuran (**50**) was irradiated in the presence of indene the coupling product **51** was obtained in 52% yields. Also in this case we obtained compound **48** as by-product.

Scheme 12



45 **46** **48**

52 **53**

In conclusion we have shown that nitroarenes react with arylalkenes to give products deriving from a transposition reaction of the adduct between the reagents (Figure 2). On the other hand, in some cases, we observed the preferential formation of products deriving from a substitution reaction on the carbon bearing the nitro group. We can see that substitution products can be obtained 1. only with 1,1-diphenylethylene and indene and 2. using a heterocyclic nitroarene. We want to attempt an explanation of this behaviour. We do not know the mechanism of the formation of the substitution products. Nevertheless, in all the systems studied (with the exception of the unreactive *trans*-stilbene) the electron transfer process is thermodynamically allowed. Then, we can suppose that the formation of the substitution products can result as a different behaviour of the radical pair deriving from the electron transfer process between the arylalkenes and the nitroarenes.

The electron transfer process involves a frontier orbital interaction. In Table 6 we have reported the energy of both the HOMOs and the LUMOs of selected reagents. These values were obtained by using AM1 semiempirical method. In all the cases the best interaction between the frontier orbitals is between the lowest SOMO of the triplet nitroarenes and the HOMO of the arylalkenes. In Figure 1 we showed that the lowest SOMOs of nitrobenzene and 2-nitrothiophene have different properties: for nitrobenzene the SOMO is localized mainly on the nitro group and in an orbital perpendicular to the aromatic ring. However, for 2-nitrothiophene the lowest SOMO is mainly localized on the aromatic ring and showed a π character. Furthermore, calculations performed on styrene showed that this molecule did not have a dipolar moment (μ = 0.048 D).

Figure 2

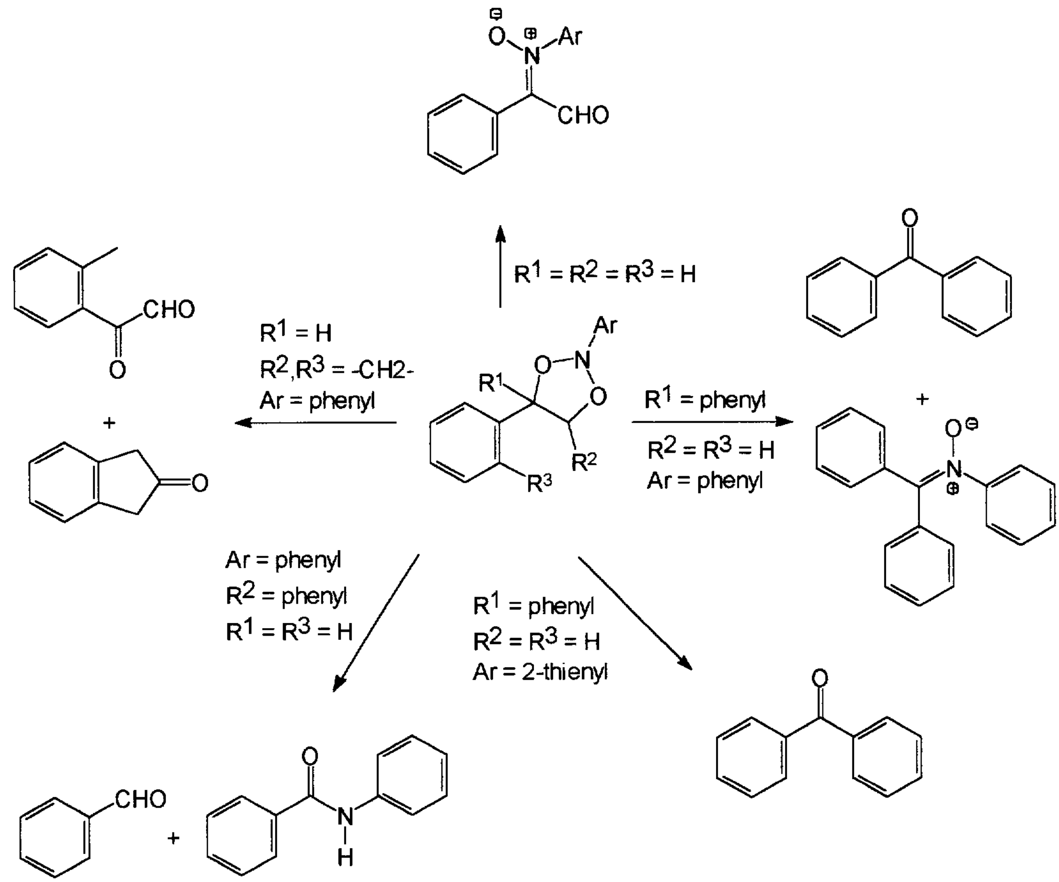


Table 6 - HOMO and LUMO for the used reagents.

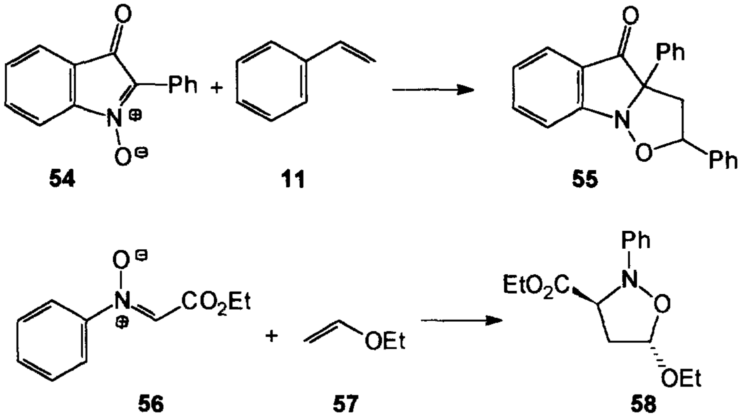
Reagents	Electronic State	lowest SOMO (eV)	highest SOMO (eV)	HOMO (eV)	LUMO (eV)
Nitrobenzene	T_1	- 8.43	- 5.66		
2-Nitrothiophene	T_1	- 8.06	- 5.40		
Styrene	S_0			- 8.80	- 0.16
Indene	S_0			- 8.66	- 0.08

In this case nitrobenzene can approach styrene in the same plane of the molecule and 2-nitrothiophene in a parallel plane without obstacles to give the interactions between frontier orbitals depicted in Figure 3. These interactions allow the formation, after the electron transfer process, of the adduct. On the contrary, when indene is used as substrate, the low dipole moment of the molecule (μ = 0.539 D) can induce an interaction between frontier orbitals where the alignment of the dipoles is required. The case of 2-nitrothiophene (μ = 5.343 D) is depicted in Figure 4 and we can see that, in this case, after the electron transfer process, the steric disposition of the molecules does not allow the formation of the adduct and, probably, allows the substitution reaction.

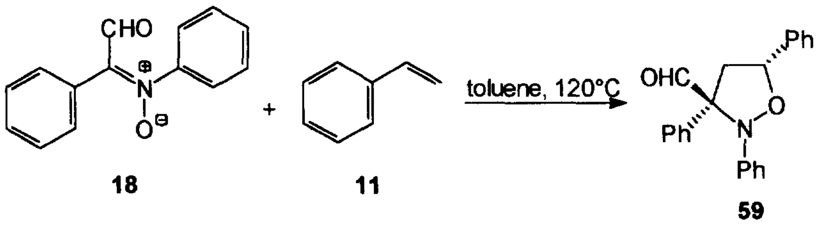
To confirm this hypothesis, we can see that 1,1-diphenylethylene showed a dipole moment (μ = 0.133 D) between styrene and indene. This datum is in agreement with the experimental results where we obtained both the products deriving from the formation of the adducts between the arylalkene and the nitroarenes and the products deriving from a substitution reaction on the carbon bearing the nitro group.

Finally, we want to report our first attempts to study the synthetic applications of the above described reactivity. We attempted to use the nitrones obtained in the reactions between nitroarenes and styrene in the synthesis of isooxazolidines through a 1,3-dipolar cycloaddition reaction. The synthesis of isooxazolidines *via* this type of reactions is a well known procedure; however, only few data are available on the behaviour of C-carbonyl substituted nitrones. The only examples available are reported in Scheme 13.[56,57]

Scheme 13



We used as starting material the nitrones obtained in the reaction between nitrobenzene and styrene; the nitrone **18**, thus obtained, was dissolved in toluene and stirred at 120°C in the presence of styrene. After five days we obtained the isooxazolidine **59** in low yields (25 - 30%).



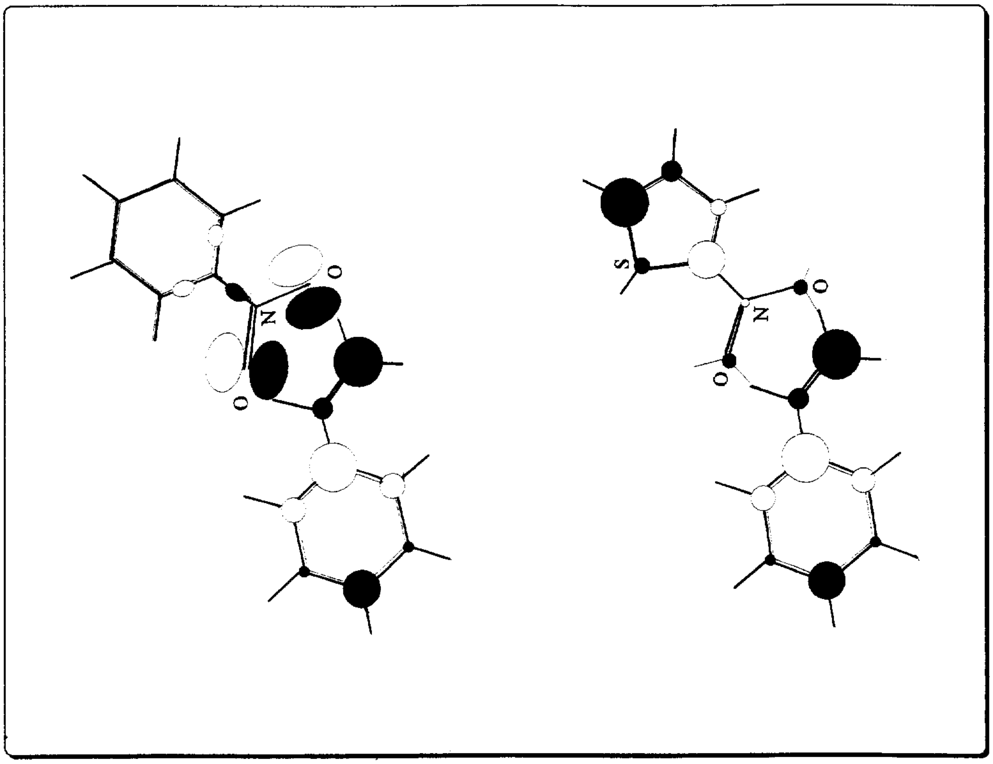


Figure 3 - Interaction between frontier orbitals in the case of styrene

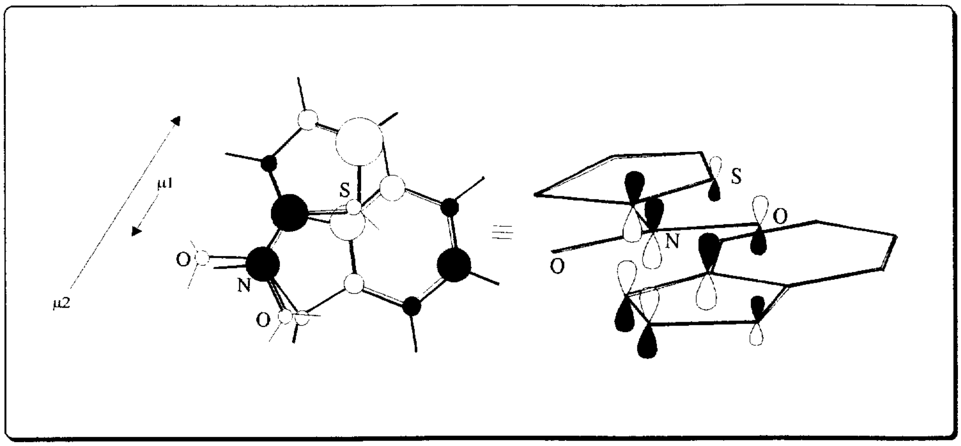


Figure 4 - Interaction between frontier orbitals of indene and 2-nitrothiophene

Nevertheless, we have to note the high stereoselectivity of this reaction that gave only one product with the above described stereochemistry. Unfortunately, our efforts devoted to extend this reaction to other alkenes failed. Both ethyl acrylate (electron withdrawing substituent on the alkene) and ethoxyethylene (electron donating substituent on the alkene) did not give the coupling reaction. We want to note that the observed reaction is in agreement with Hauck's theory. In Table 7 we have reported the calculated energy (AM1) of both the HOMO and the LUMO for the nitrone **18** and for styrene.

Table 7 - HOMO and LUMO energy for the reaction between **18** and **11**

Substrate	HOMO (eV)	LUMO (eV)
18	- 8.87	- 1.58
11	- 8.80	- 0.16

The best interaction between the frontier orbitals is between the HOMO of styrene and the LUMO of the nitrone. The orbitals and the coefficients of the atomic orbitals are depicted in Figure 5. The superposition of these orbitals can account for the observed regiochemical behaviour.

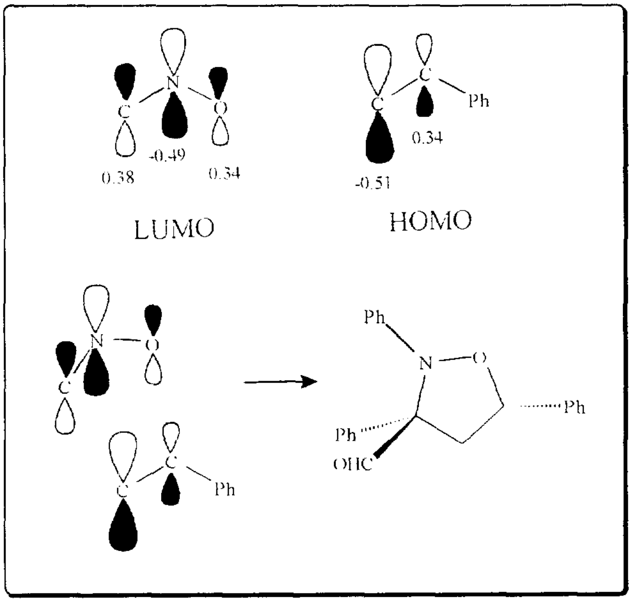


Figure 5 - HOMO of styrene and LUMO of the nitrone **18**

Experimental

Mass spectra were obtained with a Hewlett-Packard 5971 mass selective detector on a Hewlett-Packard 5890 gaschromatograph. Gas-chromatographic analyses were obtained by using an OV-1 capillary column between 70 - 250 °C (20 °C/min). Alternatively mass spectra were obtained at 70 eV with a Kratos MS-80 instrument by direct insertion at a source temperature of 150 °C. Cary 2300 spectrophotometer was used for the UV spectra. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker 300 AM instrument.

Nitrobenzene, *p*-nitrotoluene, *p*-iodonitrobenzene, 2-nitrothiophene, and nitrofuran were obtained from Aldrich. Also styrene, 1,1-diphenylethylene, indene, and *trans*-stilbene were obtained from Aldrich. Nitrobenzene was purified by extraction with sulfuric acid, water, then with 5% sodium hydroxide, and finally with water; then it was distilled over P_4O_{10}.

Voltammograms were obtained on an Amel Model 472 (Amel, Milano, Italy) polarograph equipped with a potentiostatic control, allowing potential scan rates up to 200 mV s^{-1}. As a stationary working electrode the Metrohm 6.0302.000 platinum electrode was used, while a mercury pool was used as the counter electrode. Finally, potential values were referred to an Ag, AgCl/LiCl$_{sat}$ (in acetonitrile) reference electrode whose potential value *vs* the aqueous SCE is - 124 mV (at 27°C). The experiments were carried out in acetonitrile containing $NaClO_4$ (0.114 M) as supporting electrolyte. The experiments were performed at room temperature (from 25 to

28°C) on 25 ml of the solution. The solutions to be processed were first bubbled with nitrogen for a few seconds, and then a nitrogen atmosphere was maintained above the solution in order to prevent contact with air.

2-Iodo-5-nitrothiophene (**10**). At - 5°C under stirring, nitric acid (d = 1.52, 21 g) was added to acetic anhydride (67 ml). At - 10°C 2-iodothiophene[58] (35 g) dissolved in acetic anhydride (30 ml) was added dropwise. The mixture was stirred at - 10°C for 2 h and then poured into ice water. The product precipitated and then was filtered and crystallized from MeOH (30 g, 70%); m.p. 74 -76°C (lit.,[11] 75 - 77°C); MS, *m/z* 257 (5%), 256 (6), 255 (100), 225 (11), 197 (20), 165 (6), 127 (14), 112 (12), 92 (43), 82 (59), 81 (21), 70 (12), 69 (11), and 57 (8).

4-Methyl-5-ethenylthiazole (**31**). Thiamine (10 g) was mixed with a saturated aqueous solution of hydrobromic acid (100 ml) in a sealed tube. The tube was heated at 100°C for 12 h. The solution was concentrated at reduced pressure. The solution was diluted with water. The mixture was treated with potassium carbonate and extracted with ether. The ethereal solution was dried over sodium sulfate and distilled at reduced pressure to give 4-methyl-5-(2-bromoethyl)thiazole (11 g): b.p. 86-88°C/2 mmHg. This compound was dissolved in a 36% solution of trimethylamine in benzene (50 ml). The solution was heated in a sealed tube at 100°C for 12 h. The product was filtered, washed with ether, and dried to give [2-(methyl-5-thiazolyl)ethyl]trimethylammonium bromide (10 g): m.p. 227-228°C. The product was dissolved in water (30 ml) and treated with 15 g of silver oxide. The suspension was stirred for 1 h and filtered. The filtrate was treated with potassium hydroxide (6 g). The solution was refluxed for 0.5 h. The mixture was extracted with ether and distilled at reduced pressure to give **31** (2.5 g): b.p. 64-66°C/10 mmHg (lit.,[59] 76-78°C/21 mmHg); ^{1}H NMR ($CDCl_3$) δ: 8.57 (s, 1 H), 6.82 (dd, 1 H), 5.27 (m, 2 H), and 2.35 ppm (s, 3 H).

Photochemical irradiation of nitroarenes in the presence of styrene. C-Phenyl-C-formyl-N-phenyl-nitrone (**18**). Nitrobenzene (210 mg) was dissolved in acetonitrile (70 ml) in the presence of styrene (5 g). The oxygen was removed by fluxing the solution with nitrogen for 1 h and then the solution was irradiated with a 125 W high-pressure mercury arc (Helios-Italquartz) surrounded by a Pyrex water jacket. After 2 h, the solvent was evaporated and the crude product was chromatographed on SiO_2. Elution with *n*-hexane - Et_2O (9:1) gave pure **18** (280 mg, 73%). Very viscous oil. ^{1}H NMR ($CDCl_3$) δ: 10.00 (s, 1 H), 7.86 (d, 2 H, J = 8 Hz), 7.61 (dd, 1 H, $J_1 = J_2$ = 8 Hz), 7.58 (dd, 1 H, $J_1 = J_2$ = 8 Hz), 7.50 (dd, 3 H, $J_1 = J_2$ = 8 Hz), 7.3 (m, 2 H), and 7.0 ppm (m, 1 H). IR (ν_{max} cm^{-1}): 1685. MS, *m/z* 226 (4%), 225 (28), 207 (7), 184 (5), 182 (24), 181 (19), 180 (28), 132 (5), 131 (8), 118 (12), 117 (100), 115 (10), 105 (10), 104 (22), 103 (8), 93 (18), 92 (8), 91 (58), 78 (10), 77 (54), 65 (5), 64 (8), 51 (11).

C-Phenyl-C-formyl-N-(2-thienyl)-nitrone (**13**). Very viscous oil. ^{1}H NMR ($CDCl_3$) δ: 10.01 (s, 1 H), 7.88 (d, 2 H, J = 8 Hz), 7.61 (m, 1 H), 7.52 (dd, 3 H, $J_1 = J_2$ = 8 Hz), and 7.29 ppm (m, 2 H). IR (ν_{max} cm^{-1}): 1683. MS, *m/z* 189 (5%), 188 (17), 187 (100), 186 (79), 185 (22), 184 (13), 172 (13), 171 (14), 154 (49), 153 (79), 152 (21), 141 (16), 128 (14), 115 (11), 103 (13), 97 (26), 93 (20), 92 (10), 91 (12), 77 (18).

C-Phenyl-C-formyl-N-(2-furyl)-nitrone (**16**). Very viscous oil. ^{1}H NMR ($CDCl_3$) δ: 9.98 (s, 1 H), 7.86 (d, 2 H, J = 8 Hz), 7.59 (d, 1 H, J = 5 Hz), 7.50 (dd, 3 H, $J_1 = J_2$ = 8 Hz), 7.44 (m, 1 H), and 7.37 ppm (m, 1 H). IR (ν_{max} cm^{-1}): 1685. MS, *m/z* 171 (13%), 170 (98), 169 (37), 142 (22), 141 (100), 139 (13), 116 (9), 115 (55), 77 (5), 63 (8).

C-Phenyl-C-formyl-N-(5-iodo-2-thienyl)-nitrone (**12**). Very viscous oil. ^{1}H NMR ($CDCl_3$) δ: 10.00 (s, 1 H), 7.86 (d, 2 H, J = 8 Hz), 7.50 (dd, 3 H, $J_1 = J_2$ = 8 Hz), and 7.32 ppm (m, 2 H), IR (ν_{max} cm^{-1}): 1680. MS, *m/z* 314 (6%), 313 (14), 312 (100), 185 (9), 184 (31), 153 (9), 152 (69), 141 (16), 139 (9), 128 (8), 115 (12), 92 (9).

C-Phenyl-C-formyl-N-(p-tolyl)-nitrone (**21**). Very viscous oil. ^{1}H NMR ($CDCl_3$) δ: 10.02 (s, 1 H), 8.12 (d, 2 H, J = 8 Hz), 7.90 (d, 2 H), 7.61 (dd, 1 H, $J_1 = J_2$ = 8 Hz), 7.56 (dd, 3 H, $J_1 = J_2$ = 8 Hz), 7.30 (m, 1 H), 7.05 (m, 1

H), and 2.45 ppm (s, 3 H). MS, *m/z* 240 (12%), 239 (59), 222 (8), 221 (56), 220 (100), 210 (50), 194 (6), 162 (6), 235 (8), 134 (70), 118 (7), 117 (22), 115 (25), 104 (9), 91 (26), 89 (8), 77 (22), 65 (10), 51 (7), 39 (6).

Photochemical irradiation of 4-methyl-5-ethenylthiazole (**31**). 4-Methyl-5-ethenylthiazole (500 mg, 4 mmoles) was dissolved in acetonitrile (70 ml) in the presence of nitrobenzene (200 mg). The oxygen was removed fluxing the mixture with nitrogen for 1 h. The mixture was irradiated in an immersion apparatus with a 125 W high pressure mercury arc (Helios-Italquartz) surrounded by a Pyrex water-jacket. After 72 h, the solvent was evaporated. The crude product was chromatographed on silica gel. Elution with EtOAc gave pure product **32** (180 mg). Compound **32** crystallized from EtOAc - *n*-hexane but the compound showed a very low melting point. ^{1}H NMR ($CDCl_3$) δ: 10.8 (s, 1 H), 8.95 (s, 1 H), and 2.74 ppm (s, 3 H). ^{13}C NMR ($CDCl_3$) δ: 182.12, 161.61, 158.53, 132.74, 128.89, and 16.03 ppm. MS, *m/z* 278 (2%), 256 (10), 246 (52), 218 (30), 203 (15), 138 (77), 126 (100), 111 (57), 106 (48), 93 (20), 91 (20, and 77 (48).

Photochemical irradiation of nitroarenes in the presence of 1,1-diphenylethylene. C,C,N-terphenyl-nitrone (**35**). Nitrobenzene (201 mg) was dissolved in acetonitrile (70 ml) in the presence of 1,1-diphenylethylene (2.98 g). The mixture was irradiated with a 125 W high-pressure mercury arc (Helios-Italquartz) surrounded by a Pyrex water jacket. After 5 h, the solvent was evaporated and the crude product was chromatographed on silica gel. Elution with *n*-hexane - EtOAc 9:1 gave pure **35** (273 mg). Very viscous oil. ^{1}H NMR ($CDCl_3$) δ: 7.51 (m, 1 H), 7.47 (m, 1H9, 7.45 (m, 1 H), 7.26 (m, 5 H), 7. 24 (m, 1 H), 7.23 (m, 2 H), and 7.22 ppm (m, 4 H). MS, *m/z* 273 (13), 180 (5), 167 (16), 139 (3), 105 (100), 77 (56). In the same column chromatography 114 mg of benzophenone were obtained. MS, *m/z* 182 (57%), 165 (2), 152 (4), 105 (100), 77 (56).

C,C-Diphenyl-N-(4-iodophenyl)-nitrone (**37**). Very viscous oil. ^{1}H NMR ($CDCl_3$) δ: 7.61 (m, 1 H), 7.59 (m, 1 H), 7.29 (m, 6 H), 7.23 (m, 2 H), and 7.22 ppm (m, 4 H). MS, *m/z* 400 (10%), 399 (49), 272 (9), 203 (2), 167 (48), 166 (26), 140 (9), 139 (12), 105 (100), 77 (62), 51 (16).

1,1-Diphenyl-2-(4-iodophenyl)ethylene (**38**). Very viscous oil. MS, *m/z* 383 (4%), 382 (10), 306 (57), 254 (15), 203 (37), 179 (52), 165 (97), 77 (100).

1,1-Diphenyl-2-(5-nitro-2-thienyl)-ethylene (**39**).Very viscous oil. ^{1}H NMR ($CDCl_3$) δ: 7.80 (d, 1 H), 7.70 (d, 1 H), 7.34 (m, 5 H), 7.27 (m, 5 H), amd 6.85 ppm (s, 1 H). MS, *m/z* 307 (92%), 261 (7), 228 (100), 215 (77), 184 (17), 165 (46), 115 (34), 77 (50)

1,1-Diphenyl-2-(5-iodo-2-thienyl)-ethylene (**40**). Very viscous oil. ^{1}H NMR ($CDCl_3$) δ: 7.51 (d, 1 H), 7.45 (d, 1 H), 7.32 (m, 4 H), 7.28 (m, 4 H), 7.01 (d, 1 H), and 6.41 ppm (d, 1 H). MS, *m/z* 390 (6%), 389 (24), 388 (95), 261 (6), 260 (12), 259 (13), 258 (14), 229 (21), 228 (100), 227 (14), 226 (22), 215 (20), 202 (30), 189 (15), 184 (10), 165 (15), 163 (13), 152 (13), 139 (17), 115 (10), 77 (5).

1,1-Diphenyl-2-(2-thienyl)-ethylene (**41**). Very viscous oil. MS, *m/z* 263 (22%), 262 (100), 261 (33), 247 (11), 229 (26), 228 (28), 215 (11), 202 (15), 185 (26), 184 (24), 165 (7), 152 (11), 139 (8), 115 (6), 113 (6), 101 (4), 77 (4), 51 (4).

Photochemical irradiation of nitroarenes in the presence of trans-stilbene. N-Phenylbenzamide (**43**). Nitrobenzene (359 mg) and *trans*-stilbene (3.2 g) were dissolved in benzene (100 ml) and the oxygen was removed fluxing the solution with nitrogen for 1 h. The mixture was irradiated with a 125 W high-pressure mercury arc (Helios-Italquartz) surrounded by a Pyrex water jacket. After 24 h, the solvent was evaporated and the crude product was chromatographed on silica gel. Elution with *n*-hexane - EtOAc 9:1 gave pure benzaldehyde (40 mg) and then 21 mg of *N*-phenylbenzamide. Very viscous oil. ^{1}H NMR ($CDCl_3$) δ: 7.86 (m, 2H), 7.49 (m, 6 H), and 7.18 ppm (m, 2 H). MS, *m/z* 198 (7%), 197 (53), 106 (7), 105 (100), 77 (50), 65 (7).

Photochemical irradiation of nitroarenes in the presence of indene. 2-(o-tolyl)-2-oxo-ethanale (**45**). Nitrobenzene (215 mg) and indene (2.5 g) were dissolved in acetonitrile (100 ml) and the oxygen was removed fluxing the solution with nitrogen for 1 h. The mixture was irradiated with a 125 W high-pressure mercury arc

(Helios-Italquartz) surrounded by a Pyrex water jacket. After 24 h, the solvent was evaporated and the crude product was chromatographed on silica gel. Elution with *n*-hexane - EtOAc 9:1 gave pure **45** (180 mg). Very viscous oil. ^{1}H NMR ($CDCl_3$) δ: 9.79 (s, 1 H), 7.85 (m, 1 H), 7.55 (m, 2 H), 7.24 (m, 1 H), and 4.13 ppm (s, 3 H). MS, *m/z* 148 (6%), 147 (3), 131 (2), 121 (7), 120 (82), 119 (61), 118 (3), 105 (8), 92 (13), 91 (100), 90 (10), 89 (16), 86 (2), 77 (6), 65 (32), 51 (13), 43 (30).

2-Indanone (**46**). Very viscous oil. ^{1}H NMR ($CDCl_3$) δ: 7.29 (m, 4 H), and 3.57 ppm (s, 4 H). MS, *m/z* 133 (5%), 132 (50), 105 (9), 104 (100), 103 (43), 102 (7), 89 (2), 78 (43), 77 (20), 63 (14), 51 (32).

2-(2-thienyl)indene (**47**). Very viscous oil. ^{1}H NMR ($CDCl_3$) δ: 7.38 (m, 1 H), 7.24 (s, 1 H), 7.20 (m, 5 H), 7.02 (m, 1 H), and 3.78 ppm (s, 2 H). MS, *m/z* 200 (6%), 199 (18), 198 (100), 197 (65), 195 (4), 171 (7), 166 (8), 165 (4), 163 (4), 153 (7), 152 (15), 151 (5), 139 (7), 125 (6), 97 (6), 63 (5).

2-nitroindene (**48**). Very viscous oil. MS, *m/z* 161 (30%), 144 (2), 131 (2), 116 (11), 115 (100), 114 (11), 113 (6), 102 (7), 89 (11), 77 (6), 63 (7), 51 (3).

2-(5-iodo-2-thienyl)indene (**49**). Very viscous oil. ^{1}H NMR ($CDCl_3$) δ: 7.65 (d, 1 H, J =7 Hz), 7.47 (d, 1 H, J = 7 Hz), 7.23 (s, 1 H), 7.21 (m, 4 H), and 3.39 ppm (s, 2 H). MS, *m/z* 326 (5%), 325 (15), 324 (100), 323 (5), 198 (32), 165 (9), 153 (11), 153 (15), 151 (5), 139 (8).

2-(2-furyl)indene (**51**). Very viscous oil. ^{1}H NMR ($CDCl_3$) δ: 7.38 (m, 1 H), 7.24 (s, 1 H), 7.21 (m, 5 H), 7.16 (m, 1 H), and 3.69 ppm (s, 2 H). MS, *m/z* 183 (18%), 182 (100), 181 (35), 169 (4), 154 (17), 153 (86), 152 (52), 151 (17), 150 (6), 141 (6), 128 (8), 127 (6), 116 (5), 115 (13), 91 (9), 77 (5), 75 (5), 63 (9), 51 (5).

N-Phenyl-2,5-diphenyl-2-formylisooxazolidine (**59**). C-Formyl-C-phenyl-*N*-phenylnitrone (86 mg) and styrene (482 mg) were dissolved in toluene (10 ml) and stirred at 120°C for 5 days. The solvent was evaporated and the crude product was chromatographed on silica gel. Elution with *n*-hexane - Et_2O 9:1 gave pure **59** (30 mg). Very viscous oil. ^{1}H NMR ($CDCl_3$) δ: 10.02 (s, 1 H), 7.87 (m, 2 H), 7.60 (m, 2 H), 7.54 (m, 3 H), 7.33 (m, 6 H), 3.85 (dd, 1 H, J_1 = 11.5 Hz, J_2 = 6 Hz), 3.15 (dd, 1 H, $J_1 = J_2$ = 11.5 Hz), and 2.80 ppm (dd, 1 H, J_1 = 11.5 Hz, J_2 = 6 Hz). IR (ν_{max} cm^{-1}): 1700, 1450, and 1200.

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