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The Photochemical Behaviour of 2-EWG-Substituted Heterocycles in the presence of Alkenes and Alkynes

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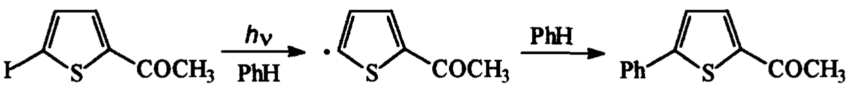
Abstract – *The photochemical reaction of some halogenoheterocycles substituted with electron withdrawing groups with acrylonitrile gave the addition product in high yields. The irradiation of 2-acetyl-5-phenylthiophene at 355 nm with a Nd:YAG laser in the presence of phenylacetylene gave 1-phenylnaphthalene, probably formed from the triplet state of phenylacetylene. 2-Acetyl-5-phenylthiophene is a sensitizer for this reaction. The irradiation of 2-nitro-5-phenylthiophene and 2-nitro-2',5-bithienyl in the presence of arylalkynes gave products from an oxidation reaction of the alkynes. The sensitization of phenylacetylene triplet can be explained assuming the population of a higher triplet state.* © 1999 Elsevier Science Ltd. All rights reserved.

Some years ago we reported some interesting results on the photochemical arylation of halogeno substituted heterocycles bearing an electron-withdrawing group.[1] This reaction has been extensively used in the synthesis of naturally occurring photobioactive thiophenes.[2] The mechanism of these reactions has been shown to occur *via* a homolytic cleavage of the carbon-iodine bond and the formation of the corresponding radical (Scheme 1).[3]

Scheme 1



The radical obtained in this reaction is an electrophilic radical. Then, the reaction of this radical with electron rich olefins was considered as a natural extension of its reactivity.[4] In these reactions the coupling product was obtained (Scheme 2).

We found subsequently that the irradiation of 2-nitrothiophene in the presence of arylalkenes gave an addition product (Scheme 3),[5] while, when 2-nitrothiophene or 2-acetylthiophene was irradiated in the presence

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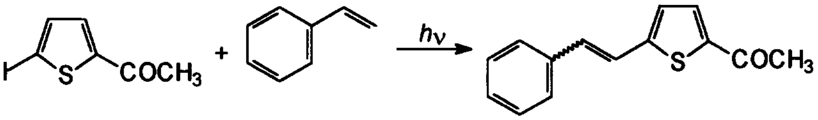
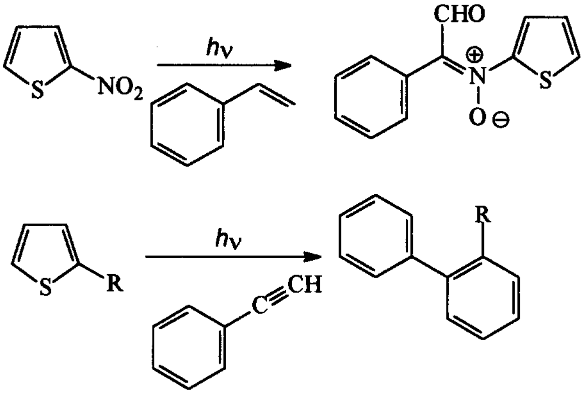
of arylalkynes, a Diels-Alder adduct was obtained, which then gave the products *via* sulfur elimination (Scheme 3).[6]

Scheme 2



Scheme 3

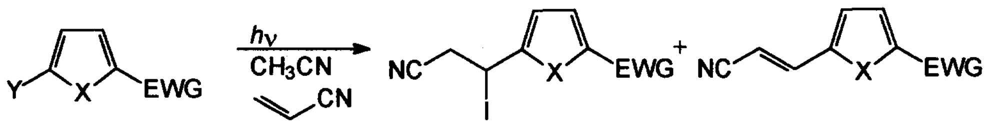


In this paper we report our results on the photochemical behaviour of some halogenoheterocycles substituted with electron-withdrawing groups, in the presence of acrylonitrile in acetonitrile as solvent. We were expecting to observe [2+2] or [4+2] photochemical cycloadditions. We have also studied the photochemical behaviour of substituted thiophenes in the presence of arylalkynes, in order to verify the capability of these substrates to give Diels-Alder adducts (or other addition products in the case of the nitro-substituted substrates). Furthermore, our heterocyclic derivatives could act as triplet sensitizers, in which case activated triplet arylalkynes could be obtained. Acetylenes are known to give some important photochemical synthetic reactions such as inter- and intra-molecular additions and cycloaddition reactions.[7-13]

Results

Halogenoheterocyclic derivatives **1a-d** reacted rapidly with acrylonitrile to give the corresponding adducts **2a-d** (Scheme 4). These products differ from the olefinic obtained using styrene or indene. Only when 2-iodo-5-nitrothiophene **1c** was used as substrate a significant amount of the olefin **3c** was obtained. The photochemical reaction of nitrothienyl derivatives with electron-rich olefins gave different products formed by addition of the nitro group to the olefin or by substitution on the nitro group.[14]

Scheme 4

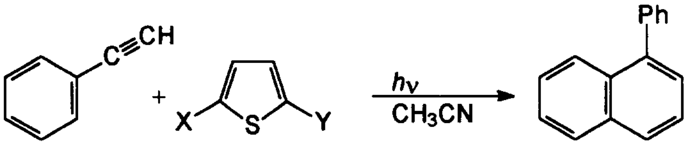


1a: X = S, Y = I, EWG = $COCH_3$	**2a** (60%)	
1b: X = S, Y = I, EWG = CHO	**2b** (55%)	
1c: X = S, Y = I, EWG = NO_2	**2c** (40%)	**3c**(34%)
1d: X = O, Y = Br, EWG = CHO	**2d** (45%)	

The reactions with alkynes were carried out by using **5a-c** as substrates (Scheme 5). Compound **5a** showed an absorption maximum at 360 nm (ε 10000 M^{-1} cm^{-1}). The triplet energy of **5a** can be estimated as *ca.* 188 kJ mol^{-1} on the basis of semiempirical calculations (PM3-RHF-CI).[15] Furthermore, this value was confirmed by stilbene isomerization.[16] 2',5-Bithienyl-2-carbaldehyde (**5b**) showed UV absorption at 389 nm (log ε 4.40) and 2-acetyl-2',5-bithienyl (**5c**) at 343 nm (log ε 4.35). 2-Nitro-5-phenylthiophene (**5d**) showed UV absorptions at 366 nm (log ε 4.21) and 248 (log ε 3.98); it did not show any fluorescence spectrum. The calculated triplet state energy is *ca.* 222 kJ mol^{-1}. Also in this case experimental determination of the triplet energy (218 kJ mol^{-1}) was in agreement with the calculated value.[16] 2-Nitro-2',5-bithienyl (**5e**) showed absorptions at 391 and 264 nm (log ε 4.26 and 3.90, respectively).

The irradiation **5a** in acetonitrile in the presence of phenylacetylene **4** with a Nd :YAG laser at 355 nm gave, after purification of the crude material on column chromatography, 1-phenylnaphthalene (**6**) as the only detectable product in 45% yield (Scheme 5).

Scheme 5



4

5a: X = Ph, Y = $COCH_3$
5b: X = 2-Thienyl, Y = CHO
5c: X = 2-Thienyl, Y = $COCH_3$

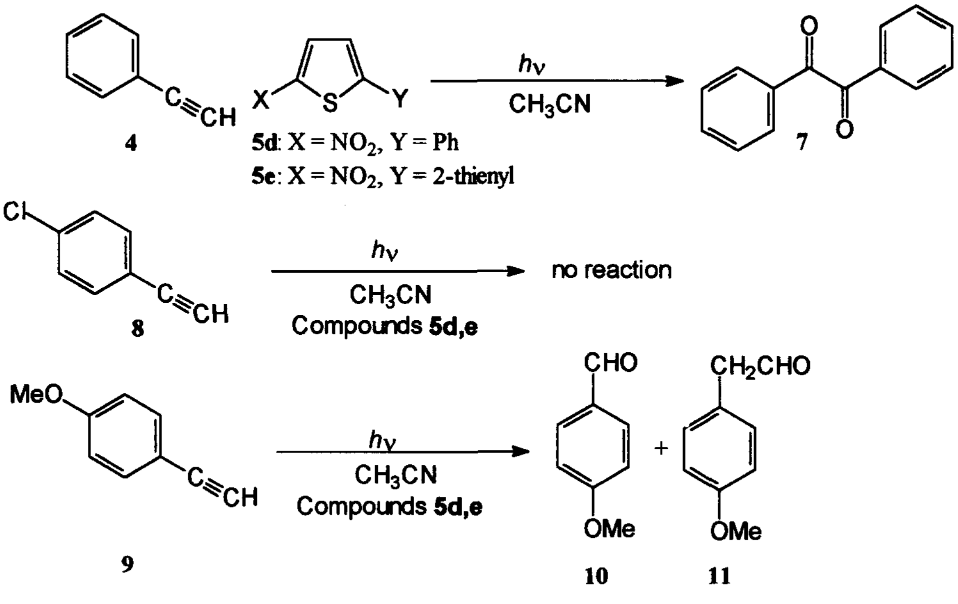
6

The same reaction did not occur using benzophenone as sensitizer. **1-Phenylnaphthalene** was also obtained as the only product using 2',5-bithienyl-2-carbaldehyde (**5b**) or 2-acetyl-2',5-bithienyl (**5c**) with phenylacetylene.

The irradiation of compound **5a** in the presence of 4-chloro- or 4-methoxy-phenylacetylene under the same experimental conditions described above did not give any reaction. Obviously, the laser irradiation of phenylacetylene gave no result as there is no absorption at 355 nm. Also the irradiation through Pyrex of **5a** in the presence of phenylacetylene using a high-pressure mercury lamp gave no result.

The irradiation of **5d** in acetonitrile in the presence of phenylacetylene with the same Nd:YAG laser at 355 nm for 4 h under argon gave benzil **7** as the only detectable product (Scheme 6, Table 2). When the same reaction was attempted by using as reagent 4-chlorophenylacetylene **8** no reaction occurred (Scheme 6, Table 2). On the contrary, if the photochemical irradiation was carried out in the presence of 4-methoxyphenylacetylene **9** a 2:1 mixture of 4-methoxybenzaldehyde **10** and 4-methoxyphenylacetaldeyde **11** was obtained (Scheme 6, Table 2). The same reaction products were obtained using as sensitizer **5e** (Scheme 6, Table 2).

Scheme 6



Discussion

The addition of radicals to double bonds has been extensively described.[17] The frontier orbital description of this type of reaction requires that the SOMO of the radical interacts with the HOMO of the olefin (usually an electron-rich one) if it is an electrophilic radical, while it requires that the SOMO of the radical interacts with the LUMO of the olefin (usually an electron-poor one) if it is a nucleophilic radical.[18] Considering the reactivity described above (the reaction with an electron-poor olefin), the radical obtained from the homolytic cleavage of carbon-halogen bond should be a nucleophilic one.

Table 2. *Photochemical irradiation of arylalkynes in the presence of nitro substituted thienyl derivatives*

Arylalkyne	Nitro thienyl derivative	Product	Yield (%)[a]
Phenylacetylene	**5d**	**7**	65
	5e	**7**	63
4-Methoxyphenylacetylene	**5d**	**10**	40
		11	22
	5e	**10**	37
		11	20

a) All the yields refer to isolated chromatographically pure products and based on amount of **5d,e**.

In order to evaluate the properties of the radical involved in the reaction, we have calculated the energy of the orbitals involved in the reaction using a semiempirical method (PM3). The results are summarized in Table 3.

Table 3. *Frontier orbitals involved in the reaction* **1** → **2**

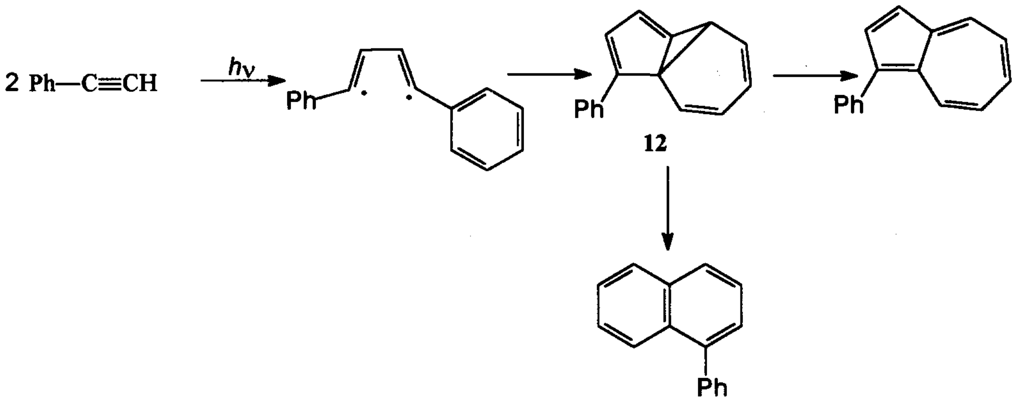
Compound	SOMO [eV]	HOMO [eV]	LUMO [eV]
5-Acetyl-2-thienyl radical	- 7.14		- 0.82
5-formyl-2-thienyl radical	- 6.62		- 0.97
5-nitro-2-thienyl radical	- 7.18		- 1.65
5-formyl-2-furyl radical	- 6.52		- 0.64
Styrene		- 9.13	- 0.12
Acrylonitrile		- 10.66	- 0.43

The best interaction can be obtained between the SOMO of the radical and the HOMO of acrylonitrile. Then, 2-acetylthiophene radical is an electrophilic radical in this reaction. Unusually, this electrophilic radical reacts efficiently with an electron-poor olefin, giving the corresponding addition product. In particular, we did not observe a difference in the reactivity in comparison with the behaviour showed by the same type of substrate in the presence of styrene.[4a] It is noteworthy that, on the basis of the HOMO energy of styrene (Table 3), the reactivity of styrene should be higher than that of acrylonitrile.

1-Phenylnaphthalene can be obtained by direct photolysis of phenylacetylene as a by-product of 1-phenylazulene, presumably *via* the intermediate **12** (Scheme 7).[19] In our experiments we did not find any indication for the presence of 1-phenylazulene in the reaction mixture.

In order to give an explanation of the above-described anomalous behaviour, the first problem we have to solve is the nature of the photochemical process involved in these reactions. The simplest hypothesis needs the presence of an energy transfer process, with the sensitized formation of the triplet acetylenes. Semiempirical calculations (PM3-RHF-CI) on the acetylenes did not allow this simple hypothesis because the triplet energy for phenylacetylene can be assumed to be at *ca.* 226 kJ mol^{-1}. We examined the hypothesis of an electron transfer process. In order to estimate the capability of our molecules to give electron transfer processes, the oxidation and reduction potentials of our substrates can give useful information. Phenylacetylene showed an anodic signal at 2.35 V. However, 2-acetyl-5-phenylthiophene did not show any cathodic signal. It showed only an anodic signal at 1.69 V.

Scheme 7



The only explanation for our results is that the laser irradiation was able to populate a triplet state at higher energy than the lowest one and that this triplet state was able to give an energy transfer process with phenylacetylene giving its triplet state.

The unreactivity of 4-chloro- and 4-methoxy-phenylacetylene can be explained on the basis of this hypothesis. In fact, the calculated triplet energy for these compounds is higher than the triplet energy of phenylacetylene, *ca.* 293 kJ mol^{-1} for 4-methoxyphenylacetylene and 297 kJ mol^{-1} for the 4-chloro derivative. Probably, the higher triplet state of compound **5a** is not sufficient high in energy to give an efficient energy transfer process with these arylalkynes.

The same type of problems discussed below characterise the reactivity of 2-nitro-5-phenylthiophene with arylalkynes. In fact, it is reported in the literature that nitro compounds can give addition reactions to olefins;[20-22] the mechanism has been described as involving an electron transfer process.[23] However, 2-nitro-5-phenylthiophene did not show any cathodic signal, but only an anodic signal at 1.87 V. Therefore an electron transfer process in our reaction mixture can be excluded. We can suppose that the reaction occurs *via* the triplet state of **5d**. The HOMO-LUMO interaction can account for the photochemical behaviour. In Table 4 we report the energy of the orbitals involved in the reaction between **5d** and phenylacetylene.

Table 4 - *Frontier orbitals of compound 5d and phenylacetylene derivatives*

Compound	S_0		T_1	
	HOMO (eV)	LUMO (eV)	LSOMO (eV)	HSOMO (eV)
2-Nitro-5-phenylthiophene			-6.56	-2.89
Phenylacetylene	-9.18	-0.23		
4-Chlorophenylacetylene	-9.10	-0.49		
4-Methoxyphenylacetylene	-8.76	-0.15		

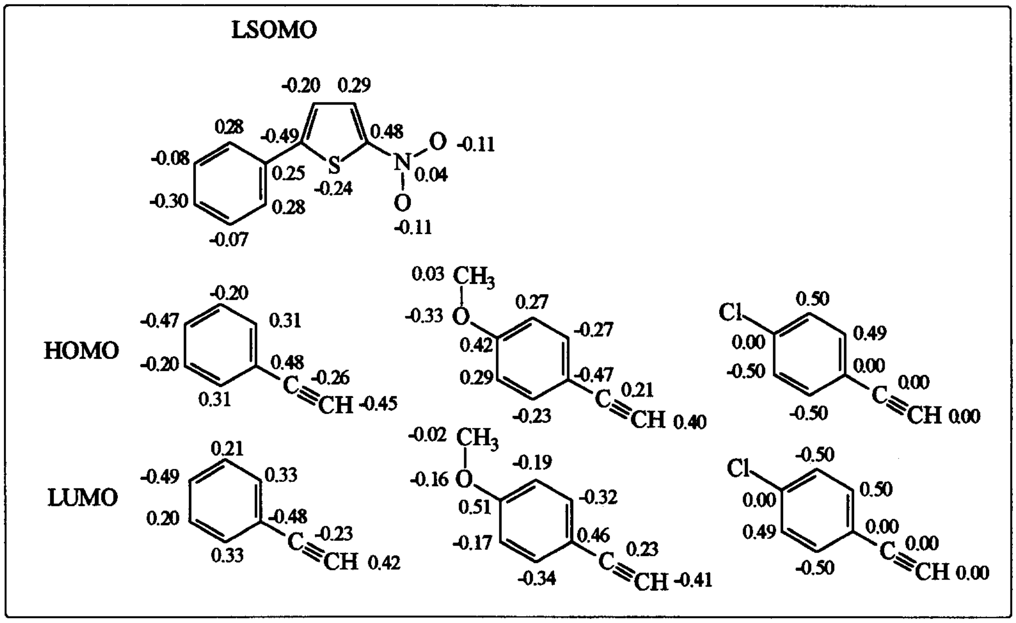


Figure 1. *Atomic coefficients of the frontier orbitals involved in the photochemical reactions of nitro derivatives with alkynes.*

We can see that the best interaction can be obtained between the LSOMO of the triplet **5d** and the HOMO of singlet phenylacetylene. The molecular orbitals involved are depicted in Figure 1. The value of the atomic coefficients shows that the interaction between the oxygen atoms of the nitro group and the acetylenic carbons is possible. On the basis of these data the best interaction can be obtained between the atoms of oxygen of the nitro group and the acetylenic carbons to give a cyclic intermediate. This intermediate is also the most stable one. In fact, the interaction between one atom of oxygen of the nitro group and one carbon of the acetylene gave the corresponding adducts, but these adducts show very high heat of formation in comparison with that of the cyclic intermediate.

This approach can be used also to justify the observed unreactivity of 4-chlorophenylacetylene under the same reaction conditions. The data reported in Table 4 show that, in this case, the best interaction is obtained between the HSOMO of the triplet **5d** and the LUMO of the acetylene. However, both the HOMO and the LUMO of 4-chlorophenylacetylene show that the value of the atomic coefficients on the acetylenic carbons is zero (Figure 1).

In conclusion, we have shown that an electrophilic radical, generated through a homolytic cleavage of a carbon-halogen bond on furan or thiophene rings substituted with electron withdrawing groups, can efficiently react with an electron-poor olefin such as acrylonitrile, giving the corresponding dehalogenated addition product. We have shown that laser irradiation of phenylacetylene in the presence of some thienyl derivatives results in the formation of 1-phenylnaphthalene, which is not due to simple energy or electron transfer. The laser irradiation of phenylacetylene derivatives in the presence of nitrothienyl derivatives gave different products depending on the nature of the phenylacetylene. These different reactions can be explained on the basis of a proposed mechanism.

Experimental

UV spectra were recorded with a Cary 2300 spectrophotometer. Mass spectra were obtained with a Hewlett-Packard 5971 mass-selective detector on a Hewlett-Packard 5890 gas chromatograph [OV-1 capillary column between 70-250 °C (20 °C min^{-1})]. NMR spectra were recorded on a Bruker 300 AM instrument. IR spectra were registered on a Perkin-Elmer 457 spectrometer. Elemental analyses were obtained by using a Carlo Erba Elemental Analyzer 1106. Phenylacetylene was obtained by Aldrich. 2-Acetyl-5-iodothiophene (**1a**),[24] 5-iodothiophene-2-carbaldehyde (**1b**),[2a] 2-iodo-5-nitrothiophene (**1c**),[25] 5-bromofuran-2-carbaldehyde (**1d**),[26] 2-acetyl-5-phenylthiophene (**5a**),[27] 2',5-bithienyl-2-carbaldehyde (**5b**),[27] 2-acetyl-2',5-bithienyl (**5c**),[28] 2-nitro-5-phenylthiophene (**5d**),[1d] and 2-nitro-2',5-bithienyl (**5e**)[1d] were prepared according to literature methods. 4-Chorophenylacetylene and 4-methoxyphenylacetylene were prepared by using the Corey's procedure.[29]

Irradiation of halogeno substituted heterocycles in the presence of acrylonitrile – General procedure - 2-acetyl-5-iodothiophene (100 mg, 0.4 mmol) was dissolved in acetonitrile (70 ml, 58 mmol) in the presence of acrylonitrile (3 g). The mixture was flushed with nitrogen for 1 h and then irradiated with a 125 W high-pressure mercury arc (Helios-Italquartz). After 1 h the mixture was washed with 0.1 N sodium thiosulfate solution and dried (Na_2SO_4). The removal of the solvent left a crude product which was chromatographed on silica gel. Elution with *n*-hexane – ethyl acetate mixtures gave pure 2-acetyl-5-(1-iodo-2-cyanoethyl)thiophene (Table 1).

2-Acetyl-5-(1-iodo-2-cyanoethyl)thiophene (**2a**) – 73 mg (60%). Viscous oil. ^{1}H NMR ($CDCl_3$) δ 7.56 (d, 1 H, J = 4 Hz), 7.05 (d, 1 H, J = 4 Hz), 4.37 (dd, 1 H, J = 7.5 and 7.0 Hz), 3.56 (m, 2 H), and 2.51 (s, 3 H); MS, *m/z* 179 (3%), 178 (4), 177 (30), 164 (8), 163 (12), 162 (100), 134 (8), 90 (17), 72 (8), 63 (10). IR ($CHCl_3$) ν_{max} 2252, 1690 cm^{-1}. C_9H_8INOS: calcd. C 35.43, H 2.64, N 4.59; found C 35.3, H 2.8, N 4.7.

5-(1-Iodo-2-cyanoethyl)thiophene-2-carbaldehyde (**2b**) – 67 mg (55%). Viscous oil. ^{1}H NMR ($CDCl_3$) δ 9.80 (s, 1 H), 7.68 (d, 1 H, J = 4 Hz), 7.17 (d, 1 H, J = 4 Hz), 4.43 (dd, 1 H, J_1 = 7.5 and 7 Hz), and 3.60 (m, 2 H); MS, *m/z* 165 (11%), 164 (12), 163 (65), 162 (100), 135 (9), 134 (10), 125 (12), 90 (12). IR ($CHCl_3$) ν_{max} 2248, 1690 cm^{-1}. C_8H_6INOS: calcd. C 33.01, H 2.08, N 4.81; found C 33.1, H 2.0, N, 4.7.

2-Nitro-5-(1-iodo-2-cyanoethyl)thiophene (**2c**) – 48 mg (40%). Viscous oil. ^{1}H NMR ($CDCl_3$) δ 7.83 (d, 1 H, J = 4 Hz), 7.04 (d, 1 H, J = 4 Hz), 4.44 (t, 1 H, J = 7 Hz), and 3.58 (d, 2 H, J = 7 Hz)); MS, *m/z* 182 (5%), 181 (7), 180 (100), 164 (7), 150 (100), 134 (25), 122 (100), 106 (12), 105 (13), 96 (20), 90 (70), 78 (35), 69 (30), 63 (40). IR ($CHCl_3$) ν_{max} 2242, 1530, 1501 cm^{-1}. $C_7H_5IN_2O_2S$: calcd. C 27.29, H 1.64, N 9.09; found C 27.2, H 1.7, N 9.1.

(E)-2-Nitro-5-(2-cyanoethenyl)thiophene (**3c**) – 24 mg (34%). Viscous oil. ^{1}H NMR ($CDCl_3$) δ 7.87 (d, 1 H, J = 4 Hz), 7.40 (d, 1 H, J = 12 Hz), 7.18 (d, 1 H, J = 4 Hz), 5.89 (d, 1 H, J = 12 Hz); MS, *m/z* 180 (22%), 170 (90), 158 (10) 141 (100), 122 (23), 90 (19), 77 (100). IR ($CHCl_3$) ν_{max} 2230, 1525, 1490 cm^{-1}. $C_7H_4N_2O_2S$: calcd. C 46.66, H 2.24, N 15.55; found C 46.6, H 2.1, N 15.7.

5-(1-Bromo-2-cyanoethyl)furan-2-carbaldehyde (**2d**) – 59 mg (45%). Viscous oil. ^{1}H NMR ($CDCl_3$) δ 9.56 (s, 1 H), 7.20 (d, 1 H, J = 3 Hz), 6.55 (d, 1 H, J = 3 Hz), 4.63 (dd, 1 H, J = 7 and 7 Hz), 3.58 (m, 2 H); MS, *m/z* 149 (2%), 148 (5), 147 (100), 146 (95), 119 (20), 92 (20), 91 (60), 90 (66), 64 (40), 63 (45). IR ($CHCl_3$) ν_{max} 2250, 1695 cm^{-1}. $C_8H_6BrNO_2$: calcd. C 42.14, H 2.65, N 6.14; found C 42.0, H 2.8, N 6.0.

Irradiation of 2-acetyl-5-phenylthiophene ***5a*** *in the presence of phenylacetylene* ***4*** - 2-Acetyl-5-phenylthiophene (10 mg) in acetonitrile (5 ml) in the presence of phenylacetylene (2 g) was irradiated with a Nd:YAG laser (Handy YAG, Quanta System, Milano, Italy) at 355 nm (*ca.* 50 mJ cm^{-2}) for 4 h. The solvent was evaporated and the crude product was chromatographed on silica gel. Elution with *n*-hexane gave 1-phenylnaphthalene as only detectable product in 45% yield.

Irradiation of 2-nitro-5-phenylthiophene ***5d*** *in the presence of phenylacetylene* ***4*** *– General procedure* - 2-Nitro-5-phenylthiophene (10 mg) in acetonitrile (5 ml) in the presence of phenylacetylene (2 g) was irradiated with a Nd:YAG laser at 355 nm for 4 h. The solvent was evaporated and the crude product was chromatographed on silica gel. Elution with *n*-hexane gave benzil as only detectable product (65%), m.p. 94-95 °C, lit.[30] m.p. 94-95 °C.
4-Methoxybenzaldehyde (**10**) – Yield 40%, b.p. 134-135 °C/12 mmHg, lit.[31] 89-90 °C/1.5 mmHg.
4-Methoxyphenylacetaldehyde (**11**) – Yield 22%, b.p. 121-122 °C/12 mmHg, lit.[32] 117.5-118 °C/9 mmHg.

Voltammograms – All voltammograms were obtained on an Amel Model 472 (Amel, Milano, Italy) polarograph equipped with a potentiostatic control, allowing potential scan rate up to 200 mV s^{-1}. As stationary working electrode the Metrohm 6.0302.000 platinum electrode was used and a mercury pool as the counter electrode. All the potential values were referred to an Ag, AgCl/LiCl$_{satd}$ (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. All experiments were performed at room temperature (25-28°C) on 25 ml of solution. The solution to be processed was first bubbled with nitrogen for few seconds, and then the nitrogen atmosphere was maintained above the solution in order to prevent contact with air. The voltammograms were recorded at a 20 mV s^{-1} scan rate unless otherwise specified.

Triplet energy measurements- A benzene solution (50 ml) containing 5 x 10^{-2} M *trans*-stilbene and 5 x 10^{-2} M of tested compounds was irradiated with a 125 W high pressure mercury arc (Helios-Italquartz) surrounded by a Pyrex water jacket for 6-8 h under nitrogen in a quartz tube surrounded by a quartz water jacket maintained at 28.0 ± 0.1 °C. The *cis-trans* ratio was determined *via* GLC and the results compared to that obtained using benzophenone as sensitizer.

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