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Applications of the photochemical reaction of iodoheterocyclic derivatives with aromatic compounds in the synthesis of new singlet oxygen sensitizers

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Abstract

Study of the photochemical coupling reaction between 2-iodo-5-nitrothiophene and indolyl derivatives indicated that the coupling reaction occurs on the C-2 position of indole to give products showing absorptions in the visible region. The photochemical reaction between iodoheterocyclic derivatives and heterocyclic allylic acetates gave the corresponding coupling products that were used as starting materials in the synthesis of polyhydroxylated compounds through reaction of the corresponding allylic alcohols with osmium tetroxide. The same reaction on 1,2-dithienylethylene or 1-(2-furyl)-2-(2-thienyl)ethylene derivatives failed. Both indolyl derivatives and polyhydroxylated compounds synthesized in this work proved to be singlet oxygen sensitizers in the photo-oxidation of *trans*-α,α'-dimethylstilbene.

Keywords: Iodoheterocyclic derivatives; Aromatic compounds; Coupling reactions; Absorption

1. Introduction

Naturally occurring thiophenes show numerous examples of photoinduced biological activity [1]. Recently, photochemical interaction between polythiophenes and supercoiled c-DNA [2,3] and photobiological activity of these molecules against viruses [4] and HIV [5] were reported. The principal target for these compounds appears to be unsaturated fatty acids in membranes, which are oxidized by singlet oxygen sensitized by polythiophene derivatives [6,7]. This behaviour is due to the hydrophobicity of the polythiophenes used.

Furthermore, polythiophene derivatives show absorptions at 300–350 nm [8]. They show very high intersystem-crossing quantum yields ($\Phi_T = 0.95$ [9]) and high efficiency in singlet oxygen generation ($\Phi_\Delta = 0.59$ [10]).

In order to synthesize both more phototoxic compounds and compounds characterized by their capability to interact with specific targets, we studied two different approaches to the synthesis of thienyl derivatives. First, a higher phototoxicity in the presence of sunlight (considered as the number of phototoxic events per unit time) could be obtained using compounds with absorptions in the visible region of the spectrum. In order to test this hypothesis, we attempted to synthesize indolyl–thienyl derivatives. Here we report the results of this research. Furthermore, in order to increase the capability of this type of molecule to interact with DNA, we attempted to synthesize polar bithienyl derivatives. Here we report our approach to the synthesis of polyhydroxylated biheterocyclic derivatives. Finally, we studied the photochemical properties of all synthesized compounds in order to establish whether they are singlet oxygen sensitizers.

2. Experimental details

2.1. Starting materials

2-Iodo-5-nitrothiophene was synthesized from thiophene, which was converted into 2-iodothiophene through reaction with iodine and HgO [11]. 2-Iodothiophene was then nitrated to give 2-iodo-5-nitrothiophene by reaction with nitric acid and acetic anhydride [12]. 5-Iodo-2-furaldehyde was obtained through reaction of 5-bromo-2-furaldehyde with KI [13]. 5-Bromo-2-furaldehyde was prepared by reaction of 2-furaldehyde with bromine in 1,2-dichloroethane [14]. 2-Acetyl-5-iodothiophene was prepared by treating 2-iodothiophene with acetic anhydride and phosphoric acid [15]. 2-(3-Acetoxyprop-1-enyl)furan was obtained by reduction of 3-(2-furyl)acrylic acid with $LiAlH_4$ and acetylation of the product. 2-(3-Acetoxyprop-1-enyl)thiophene was prepared similarly. 2-Vinylthiophene was obtained from thiophene by

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reaction with acetaldehyde and subsequent elimination [16,17]. Photochemical coupling between halothiophene or halofuran derivatives with vinyl compounds was performed as reported in Refs. [18,19].

2.2. Photochemical reaction of 2-iodo-5-nitrothiophene with indoles — general procedure

2-Iodo-5-nitrothiophene (200 mg) was dissolved in acetonitrile (70 ml) in the presence of indolyl derivatives (3.5 g). The solution was outgassed with nitrogen for 1 h and then irradiated with a 250 W high pressure mercury arc (Helios Italquartz) surrounded by a Pyrex water-jacket. After 4 h the mixture was diluted with chloroform, washed with 0.1 M sodium thiosulphate and dried. Removal of the solvent gave a crude product that was chromatographed on silica gel. Elution with 4:1 *n*-hexane–EtOAc gave pure products.

2.2.1. 2-(2-Indolyl)-5-nitrothiophene

Yield 40%. ^{1}H NMR ($CDCl_3$) δ: 7.94 (d, 1H, J 4.3 Hz, thienyl H); 7.28 (d, 1H, J 4.3 Hz, thienyl H); 7.9–7.0 (m, 5H, aromatic H). IR ν_{max}: 1525, 1333 cm^{-1}.

2.2.2. 2-(3-Methyl-2-indolyl)-5-nitrothiophene

Yield 20%. ^{1}H NMR ($CDCl_3$) δ: 7.92 (d, 1H, J 4 Hz, thienyl H); 7.7–7.0 (m, 5H, aromatic and thienyl H); 2.63 (s, 3H, CH_3). IR ν_{max}: 1530, 1350 cm^{-1}.

2.2.3. 2-(5-Bromo-2-indolyl)-5-nitrothiophene

Yield 45%. ^{1}H NMR ($CDCl_3$) δ: 7.94 (d, 1H, J 4 Hz, thienyl H); 7.22 (d, 1H, J 4 Hz, thienyl H); 7.7–7.0 (m, 4H, aromatic H). IR ν_{max}: 1530, 1330 cm^{-1}.

2.2.4. 2-(5-Methoxy-2-indolyl)-5-nitrothiophene

Yield 22%. ^{1}H NMR ($CDCl_3$) δ: 7.95 (d, 1H, J 4 Hz, thienyl H); 7.22 (d, 1H, J 4 Hz, thienyl H); 8.2–6.8 (m, 4H, aromatic H); 3.32 (s, 3H, OCH_3). IR ν_{max}: 1540, 1360 cm^{-1}.

2.3. Hydrolysis of acetates 26 — general procedure

The acetate (1 g) was dissolved in 1 M methanolic KOH (100 ml) and stirred at room temperature for 24 h. Then the mixture was extracted with Et_2O and washed with water. Neutral extracts were dried over sodium sulphate. Removal of the solvent gave pure products.

2.3.1. 5'-(Prop-1-en-3-ol-1-yl)-2,2'-bifuran-5-carbaldehyde

Yield 80%. Oil. ^{1}H NMR ($CDCl_3$) δ: 9.57 (s, 1H, CHO); 7.27 (d, 1H, J 4 Hz, furyl H); 6.85 (d, 1H, J 4 Hz, furyl H); 6.70 (d, 1H, J 4 Hz, furyl H); 6.43 (s, 2H, CH=CH); 6.33 (d, 1H, J 4 Hz, furyl H); 4.33 (m, 2H, CH_2); 2.0 (bs, 1H, OH). IR ν_{max}: 3605, 3440, 1706, 1688, 1615, 1600, 1524, 1450, 1397, 1374, 1271, 1020, 958 cm^{-1}.

2.3.2. 5'-(Prop-1-en-3-ol-1-yl)-5-acetyl-2,2'-bithiophene

Yield 83%. Oil. ^{1}H NMR ($CDCl_3$) δ: 7.62 (d, 1H, J 4 Hz, thienyl H); 7.53 (d, 1H, J 4 Hz, thienyl H); 7.13 (m, 2H, CH=CH); 7.04 (d, 1H, J 4 Hz, thienyl H); 6.72 (d, 1H, J 4 Hz, thienyl H); 3.68 (t, 2H, J 6 Hz, CH_2); 2.50 (s, 3H, CH_3); 2.2 (bs, 1H, OH). IR ν_{max}: 3400, 1650, 1467, 1432, 1275, 1034, 927 cm^{-1}.

2.3.3. 2-Acetyl-5-[5-(prop-1-en-3-ol-1-yl)-2-furyl]-thiophene

Yield 80%. Oil. ^{1}H NMR ($CDCl_3$) δ: 7.60 (d, 1H, J 4 Hz, thienyl H); 7.55 (d, 1H, J 4 Hz, thienyl H); 6.74 (d, 1H, J 4 Hz, furyl H); 6.51 (m, 2H, CH=CH); 6.36 (d, 1H, J 4 Hz, furyl H); 4.30 (m, 2H, CH_2); 2.50 (s, 3H, CH_3); 2.0 (bs, 1H, OH). IR ν_{max}: 3400, 1660, 1450, 950 cm^{-1}.

2.3.4. 2-[5-(Prop-1-en-ol-1-yl)-2-thienyl]furan-5-carbaldehyde

Yield 75%. Oil. ^{1}H NMR ($CDCl_3$) δ: 9.60 (s, 1H, CHO); 7.24 (d, 1H, J 4 Hz, furyl H); 7.10 (m, 2H, CH=CH); 7.00 (d, 1H, J 4 Hz, thienyl H); 6.95 (d, 1H, J 4 Hz, furyl H); 6.65 (d, 1H, J 4 Hz, thienyl H); 3.72 (m, 2H, CH_2); 2.3 (bs, 1H, OH). IR ν_{max}: 3500, 1690, 1600, 1440, 960 cm^{-1}.

2.4. Reaction of compounds 27 with osmium tetroxide — general procedure

The allylic alcohol **27** (100 mg) was dissolved in 1:8 water–acetone mixture (40 ml) and treated with *N*-methylmorpholine *N*-oxide (108 mg) and then with 0.02 mmol of ^{t}BuOH solution of osmium tetroxide. The mixture was stirred overnight and then quenched with $NaHSO_3$. After stirring for 10 min, the mixture was extracted with EtOAc and dried (Na_2SO_4). Preparative thin layer chromatography (TLC) gave pure products.

2.4.1. 5'-(Prop-1,2,3-triol-1-yl)-2,2'-bifuran-5-carbaldehyde

Yield 72%. Oil. ^{1}H NMR (CD_3OD) δ: 9.52 (s, 1H, CHO); 7.48 (d, 1H, J 4 Hz, furyl H); 6.91 (d, 1H, J 4 Hz, furyl H); 6.82 (d, 1H, J 4 Hz, furyl H); 6.53 (d, 1H, J 4 Hz, furyl H); 4.73 (d, 1H, J 5 Hz, C*H*OH–CHOH–CH_2OH); 3.92 (m, 1H, CHOH–C*H*OH–CH_2OH); 3.63 (dd, 1H, J_1 11 Hz, J_2 5 Hz, CHOH–CHOH–CH_AH$_B$OH); 3.41 (dd, 1H, J_1 11 Hz, J_2 5 Hz, CHOH–CHOH–CH$_A$$H_B$OH).

2.4.2. 5-Acetyl-5'-(prop-1,2,3-triol-1-yl)-2,2'-bithiophene

Yield 74%. Oil. ^{1}H NMR (CD_3OD) δ: 7.58 (d, 1H, J 4 Hz, thienyl H); 7.48 (d, 1H, J 4 Hz, thienyl H); 7.10 (d, 1H, J 4 Hz, thienyl H); 6.68 (d, 1H, J 4 Hz, thienyl H); 4.70 (d, 1H, J 5 Hz, C*H*OH–CHOH–CH_2OH); 3.95 (m, 1H, CHOH–C*H*OH–CH_2OH); 3.60 (dd, 1H, J_1 11 Hz, J_2 5 Hz, CHOH–CHOH–CH_AH$_B$OH); 3.44 (dd, 1H, J_1 11 Hz, J_2 5 Hz, CHOH–CHOH–CH$_A$$H_B$OH); 2.51 (s, 3H, CH_3).

2.4.3. 2-Acetyl-5-[5-(prop-1,2,3-triol-1-yl)-2-furyl]-thiophene

Yield 70%. Oil. ^{1}H NMR (CD_3OD) δ: 7.65 (d, 1H, J 4 Hz, thienyl H); 7.58 (d, 1H, J 4 Hz, thienyl H); 6.70 (d, 1H, J 4 Hz, furyl H); 6.40 (d, 1H, J 4 Hz, furyl H); 4.75 (d, 1H, J 5 Hz, C*H*OH–CHOH–CH_2OH); 3.90 (m, 1H, CHOH–C*H*OH–CH_2OH); 3.60 (dd, 1H, J_1 11 Hz, J_2 5 Hz, CHOH–CHOH–C$H_A$$H_B$OH); 3.40 (dd, 1H, J_1 11 Hz, J_2 5 Hz, CHOH–CHOH–C$H_A$$H_B$OH); 2.50 (s, 3H, CH_3).

2.4.4. 2-[5-(Prop-1,2,3-triol-1-yl)-2-thienyl]furan-5-carbaldehyde

Yield 70%. Oil. ^{1}H NMR (CD_3OD) δ: 9.55 (s, 1H, CHO); 7.20 (d, 1H, J 4 Hz, furyl H); 7.05 (d, 1H, J 4 Hz, thienyl H); 6.91 (d, 1H, J 4 Hz, furyl H); 6.68 (d, 1H, J 4 Hz, thienyl H); 4.68 (d, 1H, J 5 Hz, C*H*OH–CHOH–CH_2OH); 3.90 (m, 1H, CHOH–C*H*OH–CH_2OH); 3.65 (dd, 1H, J_1 11 Hz, J_2 5 Hz, CHOH–CHOH–C$H_A$$H_B$OH); 3.41 (dd, 1H, J_1 11 Hz, J_2 5 Hz, CHOH–CHOH–C$H_A$$H_B$OH).

2.5. trans-α,α'-Dimethylstilbene

α,α'-Dimethylstilbene was synthesized by reductive coupling of acetophenone according to literature data [20,21]. Crystallization from ethanol yielded pure *trans*-α,α'-dimethylstilbene, m.p. 102–103 °C. ^{1}H NMR ($CDCl_3$) δ: 7.2–6.9 (m, 10H); 1.89 (s, 6H).

2.6. Photo-oxidation of trans-α,α'-dimethylstilbene

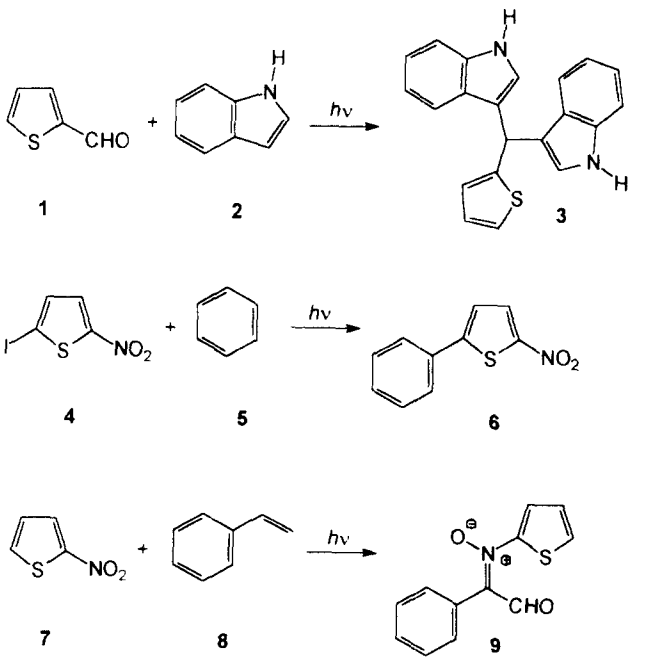
A solution (10 ml) containing 2×10^{-4} M of the sensitizer and 5×10^{-2} M *trans*-α,α'-dimethylstilbene in acetonitrile was irradiated in a Pyrex tube surrounded by a Pyrex water-jacket connected to a Haake D8-G thermostat to maintain the temperature at 13.0 ± 0.1 °C with a high pressure mercury arc (250 W, Helios Italquartz) surrounded by a Pyrex water-jacket in the presence of oxygen. In the reaction of *trans*-α,α'-dimethylstilbene with oxygen sensitized by indolyl derivatives a filter with cut-off at 400 nm was used. It was a 1% (w/v) $NaNO_2$ solution in water. After 4 h the solvent was removed at room temperature on a rotary evaporator. Residual oil was analysed via ^{1}H NMR. Compound **20** — ^{1}H NMR ($CDCl_3$) δ: 1.84 (s, 3H, CH_3); 5.49 (dd, 2H, J_1 7.9 Hz, J_2 1.0 Hz, C=CH_2); 7.0–7.5 (m, 10H). Compound **21**: the identification of this compound was made by ^{1}H NMR ($CDCl_3$) using the peak at δ 2.30 (s, 3H, CH_3). Compound **22** was determined by ^{1}H NMR of the reaction mixture in benzene-d_6 using the peaks at δ 1.23 (s, 3H, CH_3) and 1.62 (s, 3H, CH_3). Compound **23** was determined by ^{1}H NMR of the reaction mixture in benzene-d_6 using the peak at δ 1.70 (s, 3H, CH_3). Compound **20** was also isolated from the reaction mixture by column chromatography on silica gel. Elution with 9:1 *n*-hexane–EtOAc gave pure **20** whose ^{1}H NMR spectrum was reported above.

3. Results and discussion

Some years ago we reported that the irradiation of aromatic and heteroaromatic carbonyl derivatives **1** in the presence of indole (**2**) gave analogues of triphenylmethane **3** (Scheme 1) [22]. This reaction can be explained by considering a 2+2 photochemical cycloaddition between the carbonyl group and the C2–C3 double bond of indole [23].

More recently we have reported that 2-iodo-5-nitrothiophene (**4**) gave the corresponding arylation products **6** when it was irradiated in the presence of aromatic compounds, while 2-nitrothiophene (**7**) gave a nitrone **9** when it reacted with styrene (Scheme 1) [24,25].

We decided to test the photochemical behaviour of 2-iodo-5-nitrothiophene with indole in order to obtain information on the following questions. (i) We wanted to verify whether the reaction of carbonyl derivatives with indole to give triphenylmethane analogues could be avoided by using other electron-withdrawing groups that cannot give 2+2 cycloaddition reactions. (ii) We wanted to verify whether nitrothienyl derivatives were able to undergo an addition reaction to the C2–C3 double bond of indole as described for styrene. (iii) We have shown that the presence of the nitro group shifted the absorption maximum in the UV spectrum towards the visible region in comparison with the corresponding carbonyl-substituted derivatives [24]; it is conceivable that indolyl nitrothiophene derivatives of type **6** can absorb light in the visible region; considering that compounds **6** are singlet oxygen sensitizers [24] the shift of absorption towards the visible region of the spectrum could be important in order to increase the efficiency of photobiological activity of these compounds in terms of time of exposition to have phototoxic effects [26].

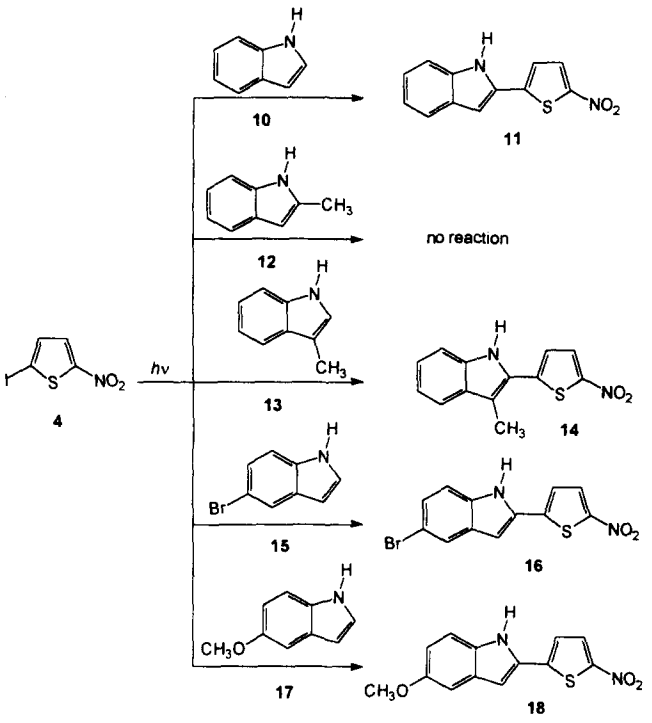


1 2 3 4 5 6 7 8 9

Scheme 1.

The irradiation of 2-iodo-5-nitrothiophene in the presence of indole in acetonitrile gave a product that was identified on the basis of ^{1}H NMR and IR spectra as the compound **11** (Scheme 2, Table 1).

The attack position of the thiophene ring on indole was identified by testing the photochemical behaviour of 2- and 3-methylindole. While 2-methylindole did not give any reaction product, 3-methylindole gave the expected product.

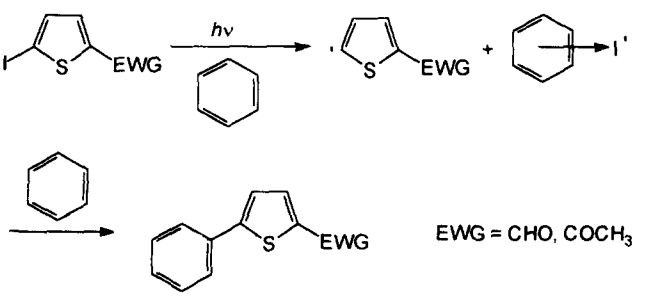


Scheme 2.

Table 1
Photochemical reaction of compound 4 with indole derivatives

Indole	Irradiation time (h)	Product	Yield (%) [a]
Indole	4	**11**	40
2-Methylindole	6	–	–
3-Methylindole	4	**14**	20
5-Bromoindole	4	**16**	45
5-Methoxyindole	4	**18**	22

[a] All the yields refer to isolated chromatographically pure compounds.



Scheme 3.

However, in this case low yields of the coupling product were obtained. We think that the low yields were due to steric effects of the methyl group.

Subsequently we tested 5-bromo- and 5-methoxyindole as starting materials. While compound **15** gave the coupling product in acceptable yields, 5-methoxyindole gave very low yields of the corresponding coupling product. Obviously in this case no steric factors can be used to justify this result.

Recently we have shown that the photochemical arylation of thienyl derivatives occurs via a triplet σ,σ^* state of the substrate; this excited state interacts with aromatic compounds to give homolytic cleavage of the C–halogen bond, with the formation of both the radical and a complex between the aromatic compound and the halogen atom (Scheme 3) [27].

The reactivity of aromatic compounds is related to their capability to give the observed complex and can be estimated on the basis of their E^{ox}. E^{ox} for indole can be estimated to be 0.94 V(SCE) (saturated calomel electrode) from the empirical relationship between ionization potential (IP) and E^{ox} [28]. IP for indole is 7.76 eV [29]. Furthermore, E^{ox} of 5-methoxyindole is 1.05 V(SCE) [30]. Thus the difference between oxidation potentials could account for the observed different reactivity.

As reported before, we obtained only products substituted on the 2 position of indole. These results are not in agreement with our previously reported data on the photochemical coupling of indoles with carbonyl-substituted compounds, where we observed the formation of C-3-substituted products only [22]. It is noteworthy that literature data on this subject are not clear. While with thermally generated benzyl radical a reaction at the 2 and 3 positions of indole was described [31], the photoinduced Friedel–Crafts reaction with methyl chloroacetate gave a mixture of indoleacetic acid derivatives where 3- and 4-substituted compounds were the major components [32]. This behaviour was confirmed by the reaction of 2-methylindole with acrilonitrile, which furnished comparable amounts of 3- and 4-substituted compounds [33]. In contrast, indole can react with 2-bromomaleic anhydride at the 2 position [34].

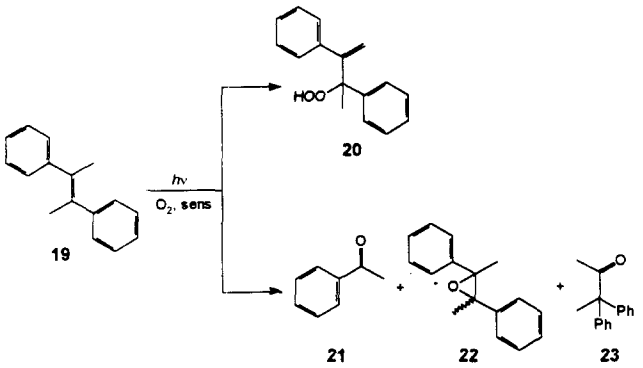
In order to establish the photochemical properties of these synthesized compounds, we have recorded their UV spectra. The results are collected in Table 2. It is noteworthy that all the compounds tested showed absorptions near 430 nm.

We used compounds **11**, **14**, **16** and **18** as substrates in the following experiments. It was reported that the irradiation of *trans*-α,α'-dimethylstilbene in acetonitrile in the presence of both oxygen and a suitable sensitizer gives only compound **20** when the sensitizer can produce singlet oxygen via an energy transfer, while if the sensitizer can give an electron transfer process, a completely different product mixture is obtained (Scheme 4) [35].

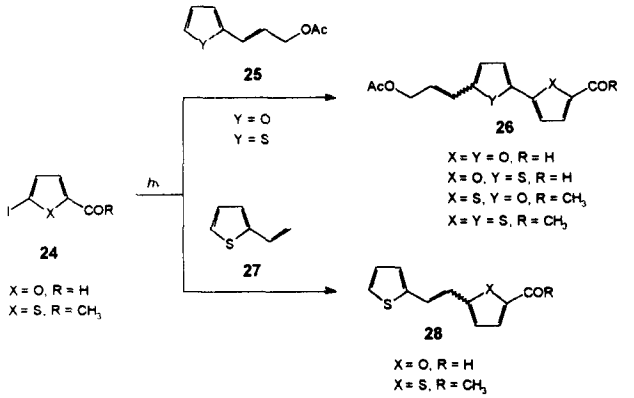
This type of reaction allows us to distinguish between type I and type II photo-oxidation [36]. The irradiation of a 5×10^{-2} M solution of **19** containing 2×10^{-4} M of sensitizer (**11**, **14**, **16** and **18**) in acetonitrile in a Pyrex tube in the

Table 2
UV absorptions of indolyl nitrothiophene derivatives

Substrate	Solvent	λ_{max} (nm)	log ϵ
11	Chloroform	430	3.69
		290	3.80
		276	3.83
14	Chloroform	430	3.71
		280	3.85
16	Chloroform	430	3.88
		288	3.79
		278	3.84
18	Chloroform	424	4.19
		300	3.91
		270	4.06



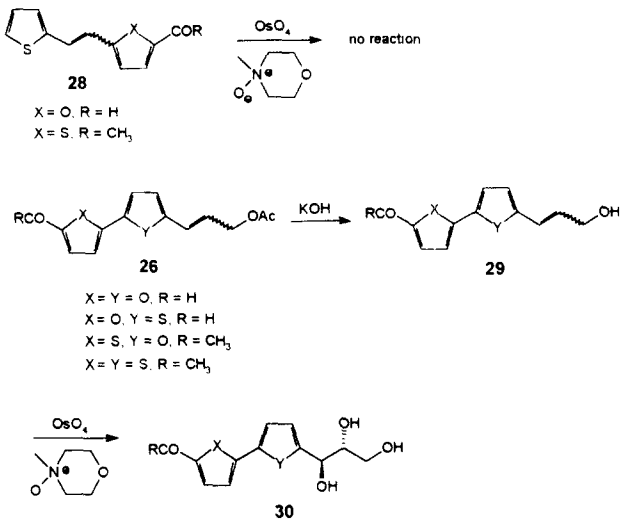
Scheme 4.



Scheme 5.

presence of a filter able to cut off wavelengths less than 400 nm at 13 °C for 4 h with a high pressure mercury arc gave a mixture which was analysed by ^{1}H NMR. In this way, only compound **20** was obtained, showing that indolyl nitrothiophene derivatives are selective singlet oxygen sensitizers. These results are not in agreement with previously reported data on the photochemical behaviour of 2-nitrothienyl derivatives. In fact, 2-nitroterthienyl was reported not to be a singlet oxygen sensitizer [5].

The second research line we have tested in this work was devoted to the synthesis of polar bithienyl derivatives in order



Scheme 6.

to increase the capability of this type of molecule to interact with DNA. We reported that the irradiation of 5-iodoheterocyclic derivatives **24** with 3-(2-thienyl)allylic acetate (**25**) gave the corresponding arylation products **26** (Scheme 5) [19]. On the other hand, the photochemical reaction of **24** with 2-ethenylthiophene (**27**) gave the corresponding substitution products on the alkene [37].

We tested the capability of these substrates to give polyhydroxylated derivatives through a reaction with osmium tetroxide. The reaction has been performed by using the catalytic procedure described by Cha et al. with *N*-methylmorpholine *N*-oxide monohydrate as oxidant [38]. Using compounds **28** as substrates, we did not obtain any product. In contrast, the allylic alcohols **29**, obtained by hydrolysis of **26**, gave the corresponding triols **30** (Scheme 6).

All the compounds **30** showed an absorption maximum in their UV spectra at 360 nm ($\epsilon = 10\,000$ M^{-1} cm^{-1}). We also tested their capability to give oxidation of *trans*-α,α'-dimethylstilbene as described before. Also in this case, when compounds **30** were used as sensitizers (Scheme 4), only the formation of compound **20** was observed, showing that these compounds are singlet oxygen sensitizers.

In conclusion, we have seen that the photochemical arylation of furan and thiophene derivatives can be used in the synthesis of compounds showing special properties. We have synthesized compounds with absorptions in the visible region and very polar compounds. All these compounds proved to be singlet oxygen sensitizers and thus potential bioactive compounds. Photobiological properties will be studied in the near future.

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