Photochemical substitution of polyhalogenothiophene and halogenothiazole derivatives †

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The irradiation of 2,3-diiodo-5-nitrothiophene in the presence of aromatic and heteroaromatic compounds gave the corresponding 2-aryl derivatives in high yields. The irradiation of 2,4-diiodo-5-nitrothiophene under the same conditions gave the corresponding 2-aryl derivatives in low yields. The observed difference in the reactivity can be explained on the basis of the hypothesis that the homolytic cleavage of the carbon–iodine bond occurred in a π,σ* triplet state. Computational results showed that the lowest triplet state of the 2,3-diiodo isomer is π,σ*, while that of the 2,4-isomer is π,π*. The irradiation of 2-bromo-5-nitrothiazole in the presence of benzene or indene gave the corresponding 2-bromo-5-arylthiazole. This behaviour can be explained by considering that the lowest excited triplet state cannot allow the cleavage of the carbon–bromine bond thus electron transfer occurs and leads to the substitution of the nitro group. The photochemical substitution reactions on 2,3-diiodo-5-nitrothiophene can be carried out in large scale using a new flow reactor using a PFTE pipe.

The photochemical reaction of halogeno substituted heterocyclic derivatives with aromatic and heteroaromatic compounds has been the object of our previous research in order to develop a synthetically useful methodology. We found that a photochemical procedure can be used in order to obtain aryl substituted furan, thiophene, pyrrole, and imidazole derivatives bearing an electron-withdrawing group starting from the corresponding halogeno substituted compounds (Scheme 1).[1–10]
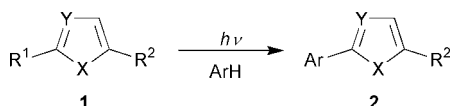
a X = O, Y = CH, R¹ = Br, R² = COR
b X = O, Y = CH, R¹ = I, R² = COR
c X = S, Y = CH, R¹ = Br, R² = COR
d X = S, Y = CH, R¹ = I, R² = COR
e X = S, Y = CH, R¹ = I, R² = CO₂R
f X = S, Y = CH, R¹ = I, R² = NO₂
g X = NH, Y = Cl, R¹ = I, R² = CHO
h X = NH, Y = N, R¹ = I, R² = NO₂

Scheme 1

In particular, we found that the presence of a nitro group in the substrates (**1f** and **1h**) allows the reaction to occur and that substrates with more that one heteroatom (**1h**) can be used in this type of reaction.

In this paper we describe the results obtained using both polyhalogeno substituted nitrothiophenes and 2-bromo-5-nitrothiazole. We studied the photochemical behaviour of these compounds in order to establish if the photochemical substitution with aromatic compounds can be used with all pentaatomic heterocyclic compounds bearing electron-withdrawing groups and if polysubstitution reaction can occur. It is relevant to note that 3,5-diiodothiophene-2-carbaldehyde gave the corresponding 3,5-diphenyl derivatives when irradiated in benzene.[4]

Finally, in order to use the above described reactions for preparative purposes, we studied a new annular reactor. In recent years several groups have directed efforts towards the design of photochemical reactors which can be used for bulk quantities. Several studies have appeared on the design of photochemical reactors[11–14] and several applications have been reported.[15–27] One of the disadvantages connected with the use of immersion photochemical reactors is the formation of deposits on the outside walls of the immersed light source. These deposits diminish and eventually halt irradiation of the reaction mixture. In such cases, periodic cleaning of the reactor is required.
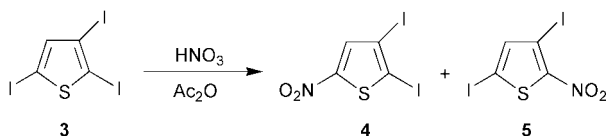
In this paper we describe a new continuous flow annular reactor based on the use of PTFE pipe.
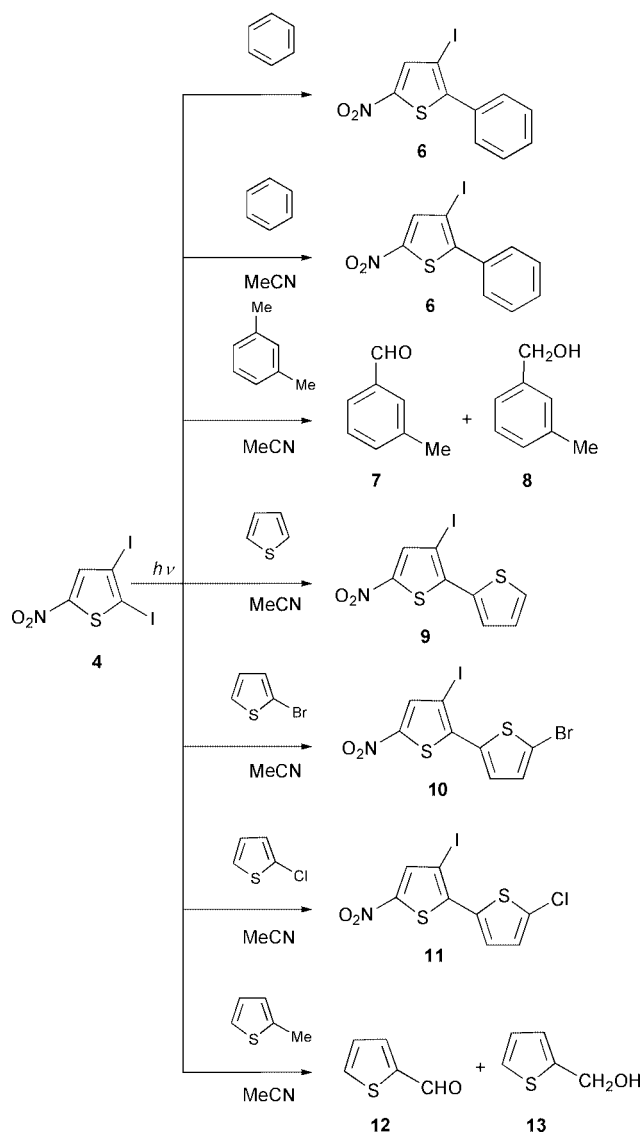
Results and discussion

In order to study the photochemical behaviour of polyhalogenothienyl derivatives, we decided to synthesise 2,3-diiodo-5-nitrothiophene (**4**) on the basis of a previous work starting from 2,3,5-triiodothiophene (**3**) *via* a nitration with nitric acid and acetic anhydride (Scheme 2).[28] In our hands this reaction not only gave **4** but also a mixture of **4** and **5** in 2:3 ratio (Scheme 2).

The irradiation of **4** in benzene gave the corresponding phenyl derivative **6** in quantitative yield (Scheme 3, Table 1). The same result was obtained by carrying out the reaction in acetonitrile in the presence of benzene. When **4** was irradiated in the presence of *m*-xylene we obtained a mixture where the only identified products were 3-methylbenzaldehyde (**7**) and 3-methylbenzyl alcohol (**8**) (Scheme 3). It is noteworthy that this is the first example where oxidation of a methyl group of an

DOI: 10.1039/b004002i

J. Chem. Soc., Perkin Trans. 1, 2000, 3513–3518 **3513**

Scheme 2

Scheme 3

Table 1 Photochemical behaviour of **4**

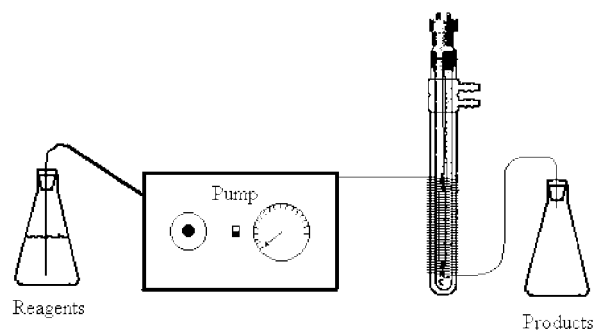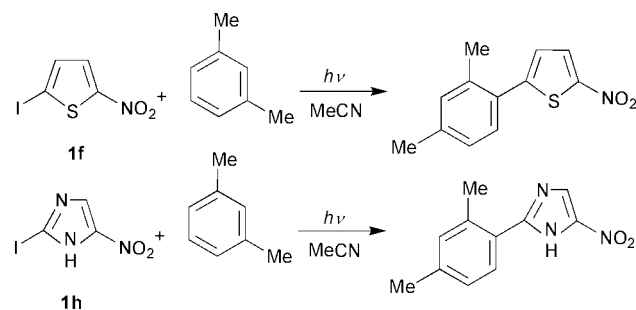| Entry	ArH	Solvent	Irradiation time/h	Product	Yield (%)
1	Benzene		24	**6**	98
2	Benzene	MeCN	24	**6**	77
3	Thiophene	MeCN	20	**9**	99
4	2-Bromo-thiophene	MeCN	20	**10**	66
5	2-Chloro-thiophene	MeCN	18	**11**	97

Fig. 1 Photochemical apparatus.

Scheme 4

We can see that the reaction of **4** in the presence of aromatic or heteroaromatic compounds works well when alkyl groups are not present in the reagent. Polysubstitution products are not obtained.

To test the possibility of performing the reaction on bulk quantities, we used as photochemical reactor the apparatus described in Fig. 1 (see Appendix). To test this apparatus we used the photochemical decarboxylation of phenylglyoxylic acid to give benzaldehyde (Scheme 5).[29] This reaction occurs
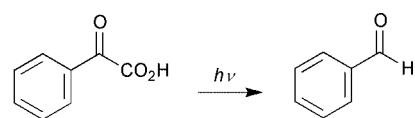
Scheme 5

with $\Phi = 0.7$. We tested the efficiency of the reactor at different fluxes of the solution of the reagent. The results are collected in Fig. 2. Maintaining the flux at *ca.* 0.1 ml min^{-1}, we observed a 90% conversion of the reagent. At 1 ml min^{-1} the observed conversion was 54%. Other reaction mixtures were irradiated in the same way and we obtained the quantitative conversion of the reagents in all the tests we performed using 0.1–1 ml min^{-1} flux range.

We did not observe the formation of films on the walls of the coil. The reactor can be used for a long time without modification of the optical properties of the coil. The coil can be used for preparative purposes. The reaction of **4** in benzene using

alkylarene was observed. In fact, 2-iodo-5-nitrothiophene (**1f**) and 2-iodo-4(5)-nitroimidazole (**1h**), irradiated in the presence of *m*-xylene, gave the corresponding 2,4-dimethyl derivatives (Scheme 4). The presence of two iodine atoms probably modifies the oxidation potential of the substrate. Calculation of the oxidation potentials of **1h** and **4** in their triplet states by using the PM3 semiempirical method gave 64.0 and 61.1 kcal mol^{-1}, respectively. These data show that the oxidation potential for 2-iodo-4(5)-nitroimidazole **1h** is higher than that of **4** and are in agreement with the experimental results where **4** gave oxidation products while **1h** did not show this type of reaction.

The irradiation of **4** in the presence of thiophene gave the corresponding bithienyl derivative **9** in quantitative yields (Scheme 3, Table 1). The same type of result was obtained using as reagent 2-bromothiophene or 2-chlorothiophene. In this case also, the bithienyl derivatives **10** and **11** were the only products recovered (Scheme 3, Table 1). In contrast, the irradiation of **4** in the presence of 2-methylthiophene gave the corresponding oxidation products **12** and **13** (Scheme 3).

Table 2 Photochemical substitution on **5**

Entry	ArH	Solvent	Irradiation time/h	Product	Yield (%)
1	Benzene	—	24	**6**	20
				14	15
2	Benzene	MeCN	36	**6**	10
				14	7
3	Thiophene	MeCN	36	**15**	8
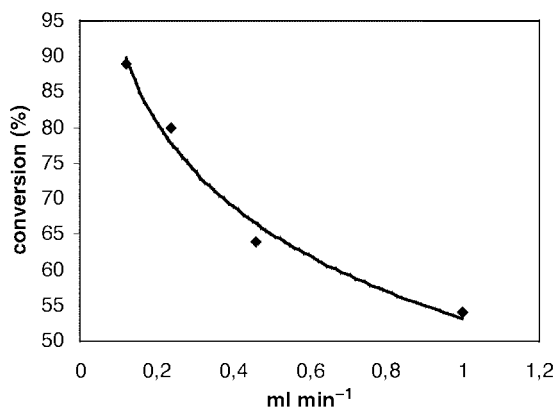
Fig. 2 Conversion of phenylglyoxylic acid.

0.1 ml min^{-1} gave quantitative formation of the product **6**. We used this reaction up to 10 g scale.

The irradiation of 2,4-diodo-5-nitrothiophene (**5**) in benzene gave 2-phenyl-3-iodo-5-nitrothiophene (**6**) and 5-phenyl-3-iodo-2-nitrothiophene (**14**) (Scheme 6, Table 2). The same result was obtained using acetonitrile as solvent (Scheme 6, Table 2). When **5** was irradiated in the presence of thiophene only very low yields of **15** were obtained (Scheme 6, Table 2). Attempts to

Scheme 6
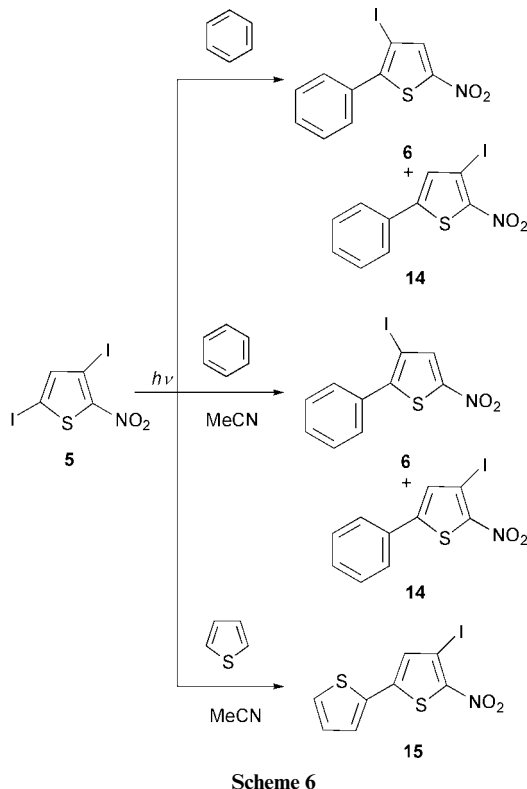
perform the reaction in the presence of 2-bromo- or 2-chloro-thiophene did not give any identifiable product.

We have to note that, while **14** is the substitution product of **5**, the conversion of **5** to **6** is surprising. Compound **6** can be

obtained only through a transposition reaction. We verified that this transposition did not occur on **4**: the irradiation of **4** in acetonitrile for 24 h did not give transposition products. This experiment ruled out all the mechanisms involved in thiophene phototranspositions.[30–32] We assume that **6** could be formed from an intermediate and we verified that a transposition reaction could occur on the radical derived from the homolytic cleavage of C–I bond (Scheme 7).

Scheme 7
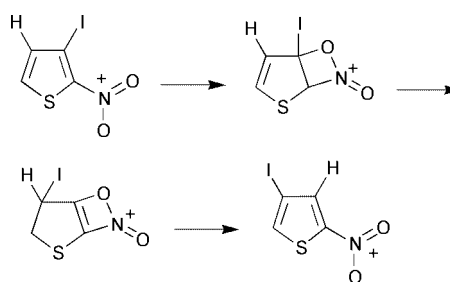
Semiempirical calculations (PM3) showed that the ΔH_f of **17** was 1.1 kcal mol^{-1} lower than that of **16**. The different stability of the radicals could be the driving force of the observed transposition.

Furthermore, it is noteworthy that **4** and **5** showed a very different reactivity in spite of the great similarity of the structures. The question is can the current hypothesis about the mechanism of this type of photosubstitution explain this behaviour. The mechanism of the photoarylation for halothiophene derivatives has been investigated.[33] Our studies showed that the excitation of the substrate leads to an n,π* triplet state, but that this excited state is unable to undergo dissociation of the carbon–iodine bond. This assertion is demonstrated by the fact that when the n,π* triplet state was generated by sensitisation with chrysene, it did not produce coupling products. Thus, the reaction probably occurs in a higher excited (π,σ*, n,σ*, or σ,σ*) triplet state mainly localised on the carbon–iodine bond. Furthermore, the interaction between this triplet state of the substrate and aromatic compounds leads to the homolytic cleavage of the C–I bond with the formation of both the radical and a complex between the aromatic compound and the halogen atom. The formation of this complex was demonstrated by the presence of a short-lived transient with λ_{max} = 510 nm showing second-order decay kinetics and a half-life of *ca.* 0.4 μs in laser flash photolysis. The thienyl radical thus formed reacts rapidly with the aromatic compound to form the corresponding arylation product (Scheme 8).[33]

Scheme 8
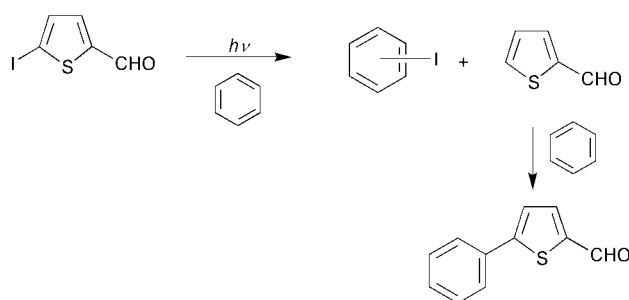
We studied the nature of the lowest triplet state in the case of compounds **1f**, **4**, and **5** using semiempirical methods (PM3). The lowest excited triplet state of **1f** showed an energy of 49 kcal mol^{-1} and it is a σ,σ* triplet state. The atomic coefficients of the orbitals involved are collected in the supplementary data (Table S1). On the basis of the above described mechanism, the homolytic cleavage of the C–I bond can occur on the lowest

excited triplet state of the molecule. The triplet state of **4** showed an energy of 48 kcal mol^{-1} and it is a $\pi,\sigma*$ triplet state (Table S1, supplementary data). Also in this case the homolytic cleavage of the C–I bond can occur in the lowest excited triplet state. Compound **5** showed a $\pi,\pi*$ triplet state at 47 kcal mol^{-1} (Table S1, supplementary data). In this case, the homolytic cleavage of the C–I bond cannot occur in the lowest excited triplet state. It needs the population of a higher triplet state and this difference could explain the observed differences in the reactivity of this compound in comparison with **1f** and **4**.

Finally we tested the photochemical behaviour of 2-bromo-5-nitrothiazole (**16**). The irradiation of **16** in benzene gave a product (**17**) where the substitution had occurred on the nitro group (Scheme 9). The yield of this reaction is low (12%). In

Scheme 9
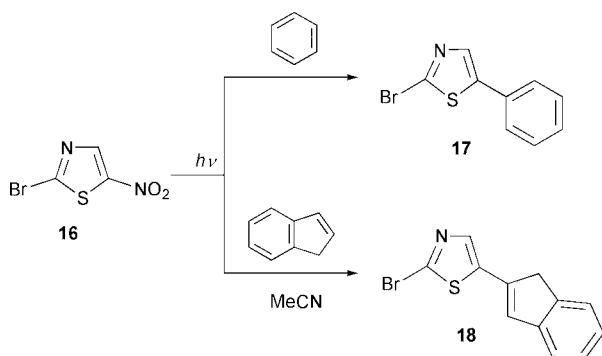
previous work we reported some examples of photochemical substitution of the nitro group.[34,35] The previous results referred to reactions between nitrothiophene derivatives and indene. This is the first result on the photochemical substitution of the nitro group in the presence of aromatic compounds. We also tested the photochemical behaviour of this substrate in the presence of indene. In this case also, the reaction occurred on the nitro group giving the corresponding coupling product **18** in reasonable yield (48%) (Scheme 9). To explain this behaviour we examined the molecular orbitals of the first excited triplet state of **16** (Table S2, supplementary data).† This is a $\pi,\pi*$ triplet state with an energy of 45 kcal mol^{-1}: this value does not allow the cleavage of the C-Br bond (ca. 66 kcal mol^{-1}). Probably, the absence of the homolytic cleavage allows the postulated electron transfer process to occur in the substitution reactions of the nitro group.[35]

In conclusion, we have shown that the photochemical substitution reactions of diiodothiophene derivatives can be carried out giving different results using different substrates. These differences can be explained on the basis of a previous reported mechanism for this type of reaction. We have also shown that 5-nitrothiazole derivatives give an interesting photochemical substitution reaction where the nitro group is the leaving group.

Experimental

Mass spectra were obtained with a Hewlett-Packard 5971 mass selective detector on a Hewlett-Packard 5890 gas chromatograph. Gas-chromatographic analyses were obtained by using an OV-1 capillary column between 70–250 °C (20 °C min^{-1}). ^{1}H NMR spectra were recorded with Bruker 300 AM instrument. J Values are given in Hz. Elemental analyses were obtained with a Carlo Erba Elemental Analyser 1106.

2,3,5-Triiodothiophene (3)

Thiophene (10.5 g), acetic acid (80 ml), water (36.9 ml), carbon tetrachloride (30 ml), sulfuric acid (2.1 ml), iodine (38.1 g), and

iodic acid (13.5 g) were refluxed for 100 h. Then water and carbon tetrachloride were added. The organic layer was washed with water, 0.1 M Na$_2$S$_2$O$_3$, and water again. The organic phase was dried over Na$_2$SO$_4$. The solvent was evaporated and the residue was crystallised from ethanol to give 2,3,5-triiodothiophene (44.5 g, 77%). Mp 83–85 °C (lit.,[36] 83–84 °C). δ_H (DMSO-d_6) 7.16 (s, 1 H).

2,3-Diiodo-5-nitrothiophene (4) and 2,4-diiodo-5-nitrothiophene (5)

2,3,5-Triiodothiophene **3** (8 g) was dissolved in acetic anhydride (40 ml). The mixture was treated with a mixture of nitric acid (d 1.52 g ml^{-1}) in acetic anhydride (40 ml) at 0 °C. The mixture was stirred for 15 min, then 0.1 M NaHCO$_3$ (100 ml) was added. The mixture was extracted with diethyl ether. The organic phase was dried over Na$_2$SO$_4$ and the solvent was evaporated. The isomers were separated using preparative TLC on 300 mg of the residue eluting with a mixture of 99 : 1 n-hexane–EtOAc. The separation gave 2,4-diiodo-5-nitrothiophene (**4**) (180 mg, 46%) and 2,3-diiodo-5-nitrothiophene (**5**) (120 mg, 31%). 2,4-Diiodo-5-nitrothiophene (**4**): δ_H 7.69 (s, 1 H); δ_C 207, 146, 85, 82; m/z 37 (4%), 69 (10), 81 (27), 97 (4), 111 (3), 127 (10), 164 (9), 208 (50), 224 (30), 238 (5), 254 (4), 323 (25), 335 (3), 351 (4), 365 (3), 381 (100) (Found: C, 12.7; H, 0.3; N, 3.5; S, 8.2. C$_4$HI$_2$NO$_2$S requires C, 12.61; H, 0.26; N, 3.68; S, 8.42%). 2,4-Diiodo-5-nitrothiophene (**5**): δ_H 7.45 (s, 1 H); m/z 37 (4%), 69 (7), 81 (29), 97 (3), 111 (3), 127 (9), 164 (5), 208 (40), 224 (50), 238 (5), 323 (4), 351 (19), 365 (2), 381 (100) (Found: C, 12.6; H, 0.2; N, 3.8; S, 8.3. C$_4$HI$_2$NO$_2$S requires C, 12.61; H, 0.26; N, 3.68; S, 8.42%).

2-Phenyl-3-iodo-5-nitrothiophene (6)

2,3-Diiodo-5-nitrothiophene **4** (100 mg) was dissolved in benzene (100 ml). The mixture was degassed with nitrogen for 10 min and then irradiated with a 125 W high pressure mercury arc (Helios-Italquartz) surrounded by a Pyrex water-jacket. At the end of the reaction (Table 1), the solvent was evaporated to give pure **6** (85 mg, 98%). δ_H 7.99 (s, 1 H), 7.7–7.5 (m, 5 H); m/z 331 (100%), 315 (2), 301 (5), 273 (3), 174 (13), 158 (77), 146 (15), 114 (32), 102 (4), 88 (7) (Found: C, 36.4; H, 1.6; N, 4.3; S, 9.7. C$_{10}$H$_6$INO$_2$S requires C, 36.27; H, 1.83; N, 4.23; S, 9.68%). When the reaction was carried out in acetonitrile the following procedure was used: 2,3-diiodo-5-nitrothiophene **4** (90 mg) was dissolved in acetonitrile (100 ml) in the presence of benzene (3 ml). The mixture was degassed with nitrogen for 10 min and then irradiated with a 125 W high pressure mercury arc (Helios-Italquartz) surrounded by a Pyrex water-jacket. At the end of the reaction (Table 1), the solvent was evaporated and the mixture was purified on preparative TLC giving 60 mg of **6** (77%).

3-Tolualdehyde (7) and 3-methylphenylmethanol (8)

2,3-Diiodo-5-nitrothiophene **4** (100 mg) was dissolved in acetonitrile (100 ml) in the presence of m-xylene (3 ml). The mixture was degassed with nitrogen for 10 min and then irradiated with a 125 W high pressure mercury arc (Helios-Italquartz) surrounded by a Pyrex water-jacket. At the end of the reaction (Table 1), the solvent was evaporated and the residue, dissolved in methanol, was analysed by GC-MS. The analysis showed the presence of **7** and **8**. 3-Tolualdehyde: m/z 120 (96%), 91 (100), 65 (9), 51 (3), 39 (5). 3-Methylphenylmethanol: m/z 122 (57%), 107 (46), 91 (50), 79 (29), 77 (29), 32 (100).

3-Iodo-5-nitro-2,2′-bithienyl (9)

2,3-Diiodo-5-nitrothiophene **4** (100 mg) was dissolved in acetonitrile (100 ml) in the presence of thiophene (3 ml). The mixture was degassed with nitrogen for 10 min and then

irradiated with a 125 W high pressure mercury arc (Helios-Italquartz) surrounded by a Pyrex water-jacket. At the end of the reaction (Table 1), the solvent was evaporated to give pure **9** (87 mg, 99%). δ_H 7.96 (s, 1 H), 7.59 (dd, 1 H, J_1 4, J_2 1), 7.54 (dd, 1 H, J_1 5, J_2 1), 7.18 (dd, 1 H, J_1 5, J_2 4); δ_C 206.7, 143.5, 137.8, 133.2, 129.6, 129.1, 128.0; *m/z* 337 (100%), 307 (6), 279 (5), 180 (5), 164 (68), 152 (8), 120 (25), 93 (4), 69 (4) (Found: C, 28.7; H, 1.1; N, 4.3; S, 19.2. $C_8H_4INO_2S_2$ requires C, 28.50; H, 1.20; N, 4.15; S, 19.02%).

3-Iodo-5-nitro-5′-bromo-2,2′-bithienyl (10)

2,3-Diiodo-5-nitrothiophene **4** (100 mg) was dissolved in acetonitrile (100 ml) in the presence of 2-bromothiophene (3 ml). The mixture was degassed with nitrogen for 10 min and then irradiated with a 125 W high pressure mercury arc (Helios-Italquartz) surrounded by a Pyrex water-jacket. At the end of the reaction (Table 1), the solvent was evaporated to give a residue that was purified *via* preparative TLC to give pure **10** (72 mg, 66%). δ_H 7.92 (s, 1 H), 7.31 (d, 1 H, *J* 1), 7.14 (d, 1 H, *J* 1); δ_C 206.8, 143.5, 137.8, 131.1, 129.6, 129.1, 128.0, 124.3; *m/z* 419 (98%), 417 (100), 385 (6), 377 (6), 306 (5), 244 (54), 163 (21), 119 (21) (Found: C, 23.0; H, 0.6; N, 3.4; S, 15.5. $C_8H_3BrINO_2S_2$ requires C, 23.10; H, 0.73; N, 3.37; S, 15.41%).

3-Iodo-5-nitro-5′-chloro-2,2′-bithienyl (11)

2,3-Diiodo-5-nitrothiophene **4** (100 mg) was dissolved in acetonitrile (100 ml) in the presence of 2-chlorothiophene (3 ml). The mixture was degassed with nitrogen for 10 min and then irradiated with a 125 W high pressure mercury arc (Helios-Italquartz) surrounded by a Pyrex water-jacket. At the end of the reaction (Table 1), the solvent was evaporated to give pure **11** (95 mg, 97%). δ_H 7.94 (s, 1 H), 7.35 (d, 1 H, *J* 1), 7.01 (d, 1 H, *J* 1); δ_C 206.7, 142.4, 137.7, 137.7, 132.0, 128.8, 127.0, 124.2; *m/z* 373 (43%), 372 (13), 371 (100), 341 (10), 313 (6), 200 (39), 199 (10), 198 (95), 186 (9), 163 (22), 119 (32), 93 (9), 69 (9) (Found: C, 26.0; H, 1.0; N, 3.7; S, 17.3. $C_8H_3ClINO_2S_2$ requires C, 25.86; H, 0.81; N, 3.77; S, 17.26%).

Thiophene-2-carbaldehyde (12) and 2-thienylmethanol (13)

2,3-Diiodo-5-nitrothiophene **4** (100 mg) was dissolved in acetonitrile (100 ml) in the presence of 2-methylthiophene (3 ml). The mixture was degassed with nitrogen for 10 min and then irradiated with a 125 W high pressure mercury arc (Helios-Italquartz) surrounded by a Pyrex water-jacket. At the end of the reaction (Table 1), the solvent was evaporated and the residue, dissolved in methanol, was analysed by GC-MS. The analysis showed the presence of **12** and **13**. Thiophene-2-carbaldehyde **12**: *m/z* 112 (100%), 83 (13), 58 (10), 39 (17). 2-Thienylmethanol **13**: *m/z* 114 (100%), 97 (67), 85 (72), 69 (9), 53 (10), 45 (30).

Flow reactor

The efficiency of the annular reactor was determined by testing it with the photochemical decomposition of phenylglyoxylic acid. A 0.1 M solution of phenylglyoxylic acid in acetonitrile–water (3:1) (10 ml) was irradiated. The mixture was then extracted with CH_2Cl_2 and dried (Na_2SO_4). The removal of the solvent gave a crude product that was dissolved in $CDCl_3$ and analysed by ^{1}H NMR. The chemical conversion was calculated from the integrated *ortho* protons of the phenyl ring of phenylglyoxylic acid at δ 8.1 and of benzaldehyde at δ 7.9 ppm with reference to the *meta* and *para* ring protons at δ 7.6 ppm. Φ is assumed to be 0.7.

2-Phenyl-3-iodo-5-nitrothiophene (6) and 5-phenyl-3-iodo-2-nitrothiophene (14)

2,4-Diiodo-5-nitrothiophene **4** (100 mg) was dissolved in ben-

zene (100 ml). The mixture was degassed with nitrogen for 10 min and then irradiated with a 125 W high pressure mercury arc (Helios-Italquartz) surrounded by a Pyrex water-jacket. At the end of the reaction (Table 2), the solvent was evaporated and the residue was purified through preparative TLC giving **6** (17 mg, 20%) and **14** (13 mg, 15%). 5-Phenyl-3-iodo-2-nitrothiophene **14**: δ_H 7.7–7.5 (m, 5 H), 7.42 (s, 1 H); *m/z* 331 (100%), 315 (7), 301 (7), 273 (18), 241 (11), 207 (11), 174 (6), 158 (61), 146 (21), 128 (11), 114 (25), 102 (11), 77 (10) (Found: C, 36.2; H, 1.9; N, 4.2; S, 9.9. $C_{10}H_6INO_2S$ requires C, 36.27; H, 1.83; N, 4.23; S, 9.68%). When the reaction was carried out in acetonitrile the following procedure was used: 2,4-diiodo-5-nitrothiophene **4** (90 mg) was dissolved in acetonitrile (100 ml) in the presence of benzene (3 ml). The mixture was degassed with nitrogen for 10 min and then irradiated with a 125 W high pressure mercury arc (Helios-Italquartz) surrounded by a Pyrex water-jacket. At the end of the reaction (Table 2), the solvent was evaporated and the mixture was purified by preparative TLC giving 9 mg of **6** (10%) and 6 mg of **14** (7%).

4-Iodo-5-nitro-2,2′-bithienyl (15)

2,4-Diiodo-5-nitrothiophene **4** (90 mg) was dissolved in acetonitrile (100 ml) in the presence of thiophene (3 ml). The mixture was degassed with nitrogen for 10 min and then irradiated with a 125 W high pressure mercury arc (Helios-Italquartz) surrounded by a Pyrex water-jacket. At the end of the reaction (Table 2), the solvent was evaporated and the residue was purified through preparative TLC to give **15** (6 mg, 8%). δ_H 7.56 (dd, 1 H, J_1 4, J_2 1), 7.55 (dd, 1 H, J_1 5, J_2 1), 7.38 (s, 1 H), 7.16 (dd, 1 H, J_1 5, J_2 4); *m/z* 337 (60%), 248 (62), 164 (44) (Found: C, 28.4; H, 1.2; N, 4.1; S, 19.1. $C_8H_4INO_2S_2$ requires C, 28.50; H, 1.20; N, 4.15; S, 19.02%).

2-Bromo-5-phenylthiazole (17)

2-Bromo-5-nitrothiazole **16** (100 mg) was dissolved in benzene (100 ml). The mixture was degassed with nitrogen for 10 min and then 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 residue was purified through column chromatography on basic Al_2O_3 (B I). Elution with *n*-hexane–EtOAc 99:1 gave **17** (15 mg, 12%). δ_H 8.32 (s, 1 H), 7.7–7.5 (m, 5 H); *m/z* 241 (98%), 239 (100), 160 (29), 134 (74), 116 (17), 102 (10), 89 (17) (Found: C, 45.2; H, 2.4; N, 5.9; S, 13.5. C_9H_6BrNS requires C, 45.02; H, 2.52; N, 5.83; S, 13.35%).

2-Bromo-5-(1*H*-inden-2-yl)thiazole (18)

2-Bromo-5-nitrothiazole **16** (100 mg) was dissolved in acetonitrile (100 ml) in the presence of thiophene (3 ml). The mixture was degassed with nitrogen for 10 min and then 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 residue was purified through column chromatography on basic Al_2O_3 (B I). Elution with *n*-hexane–EtOAc 99:1 gave **18** (64 mg, 48%). δ_H 8.45 (s, 1 H), 7.47 (m, 2 H), 7.32 (m, 2 H), 7.18 (s, 1 H); *m/z* 279 (98%), 277 (100), 160 (29), 134 (74), 116 (17), 102 (10), 89 (17).

Appendix

The photochemical apparatus for preparative purpose is described in the Fig. 1. The flux of the solution to be irradiated was maintained using a HPLC pump. The PTFE pipe showed an external diameter of 1.5 mm and an inner diameter of 1.0 mm. The coil around the lamp used *ca.* 5 m of the pipe. We used a 125 W high pressure mercury arc manufactured by Helios Italquartz (Milan), surrounded by a Pyrex water-jacket.

References

1 R. Antonioletti, M. D'Auria, A. De Mico, G. Piancatelli and A. Scettri, *Tetrahedron*, 1985, **41**, 3441.

2 R. Antonioletti, M. D'Auria, A. De Mico, G. Piancatelli and A. Scettri, *J. Chem. Soc.*, *Perkin Trans. 1*, 1985, 1285.

3 M. D'Auria, R. Antonioletti, A. De Mico and G. Piancatelli, *Heterocycles*, 1986, **24**, 1575.

4 R. Antonioletti, M. D'Auria, F. D'Onofrio, G. Piancatelli and A. Scettri, *J. Chem. Soc.*, *Perkin Trans. 1*, 1986, 1755.

5 M. D'Auria, A. De Mico, F. D'Onofrio and G. Piancatelli, *J. Chem. Soc.*, *Perkin Trans. 1*, 1987, 1777.

6 M. D'Auria, A. De Mico, F. D'Onofrio, D. Mendola and G. Piancatelli, *J. Photochem. Photobiol.*, *Sect. A*, 1989, **47**, 191.

7 M. D'Auria, *Gazz. Chim. Ital.*, 1994, **124**, 195.

8 M. D'Auria, in *Targets in Heterocyclic Systems*, *Chemistry and Properties*, ed. O. A. Attanasi and D. Spinelli, Italian Society of Chemistry, 1997, vol. 1, p. 277.

9 M. D'Auria, E. De Luca, G. Mauriello, R. Racioppi and G. Sleiter, *J. Chem. Soc.*, *Perkin Trans. 1*, 1997, 2369.

10 M. D'Auria, E. De Luca, G. Mauriello and R. Racioppi, *J. Chem. Soc.*, *Perkin Trans. 1*, 1998, 271.

11 A. E. Cassano, C. A. Martin, R. J. Brandi and O. M. Alfano, *Ind. Eng. Chem. Res.*, 1995, **34**, 2155.

12 J. P. Laplante, B. Lavabre and J. C. Micheau, *J. Chem. Phys.*, 1988, **89**, 1435.

13 B. Borderie, D. Lavabre, G. Levy, J. P. Laplante and J. C. Micheau, *J. Photochem. Photobiol.*, *Sect. A*, 1991, **56**, 13.

14 A. Said, M. C. Carre, M. L. Viriot and J. C. André, *J. Photochem. Photobiol.*, *Sect. A*, 1991, **61**, 253.

15 T. Sawazaki, S. Morikawa, K. Takahashi, A. Katayama, T. Kobayashi and T. Udagawa, *Jpn. Kokai Tokkyo Koho*, JP 61 187, 930, 1986 (*Chem. Abstr.*, 1987, **106**, 6807).

16 L. Teodorescu, G. Musca, E. Mocanu, H. Celetu and N. Rada, *Rom. Pat.*, 93 292, 1987 (*Chem. Abstr.*, 1988, **109**, 180 287).

17 B. Kerekes, *Hung. Teljes*, 38 852, 1986 (*Chem. Abstr.*, 1987, **106**, 205 095).

18 K. Oharu and T. Hamada, *Jpn. Kokai Tokkyo Koho*, 03 275 138, 1991 (*Chem. Abstr.*, 1992, **116**, 176 603).

19 G. F. Ribalchenko, Y. B. Shalnev and V. P. Bezsolitsen, *USSR Pat.*, 1 726 005, 1992 (*Chem. Abstr.*, 1993, **119**, 30 509).

20 B. Ullrich, *Ger. Offen*, DE 4 203 840, 1993 (*Chem. Abstr.*, 1994, **120**, 10 886).

21 K. Takehisa, *Jpn. Kokai Tokkyo Koho*, 08 57 299, 1996 (*Chem. Abstr.*, 1996, **124**, 264 293).

22 J. Cooke, G. Austin and M. J. McGarrity, *PCT Int. Appl.*, 96 35 508, 1996 (*Chem. Abstr.*, 1997, **126**, 33 600).

23 K. Suzuki, H. Sasaki and A. Yonezawa, *Jpn. Kokai Tokkyo Koho*, 08 273 954, 1996 (*Chem. Abstr.*, 1997, **126**, 67 646).

24 T. Takemura and J. Kamo, *Jpn. Kokai Tokkyo Koho*, 08 332, 372 1996 (*Chem. Abstr.*, 1997, **126**, 173 493).

25 H. P. Popp, *Eur. Pat.*, 803 472, 1997 (*Chem. Abstr.*, 1997, **127**, 352 923).

26 A. Meyer, S. Johne, H. Herrmann and D. Birus, *Ger. Offen*, DE 19 708 148, 1998 (*Chem. Abstr.*, 1998, **129**, 223 185).

27 A. Meyer, S. Johne, H. Herrmann and D. Birus, *Ger. Offen*, DE 19 744 740, 1998 (*Chem. Abstr.*, 1998, **129**, 223 186).

28 W. Steinkopf, H. F. Schmitt and H. Fiedler, *Justus Liebigs Ann. Chem.*, 1937, **527**, 237.

29 A. Defoin, R. Defoin-Straatmann, K. Hildebrand, E. Bittersmann and H. J. Kuhn, *J. Photochem.*, 1986, **33**, 237.

30 M. D'Auria, in *Targets in Heterocyclic Systems*, *Chemistry and Properties*, ed. O. A. Attanasi and D. Spinelli, Italian Society of Chemistry, 1999, vol. 2, 233.

31 M. D'Auria, *Heterocycles*, 1999, **50**, 1115.

32 M. D'Auria, *Adv. Heterocycl. Chem.*, submitted.

33 F. Elisei, L. Latterini, G. G. Aloisi and M. D'Auria, *J. Phys. Chem.*, 1995, **99**, 5365.

34 M. D'Auria, *Tetrahedron Lett.*, 1994, **35**, 633.

35 M. D'Auria, V. Esposito and G. Mauriello, *Tetrahedron*, 1996, **52**, 14253.

36 S. Gronowitz and V. Vilks, *Ark. Kemi*, 1963, **21**, 191.