

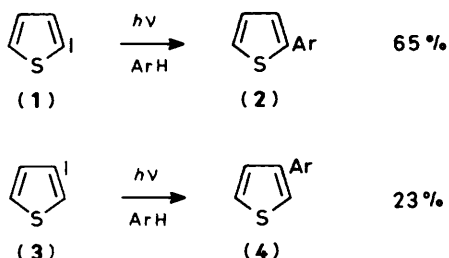
Photochemical Synthesis of Phenyl-2-thienyl Derivatives

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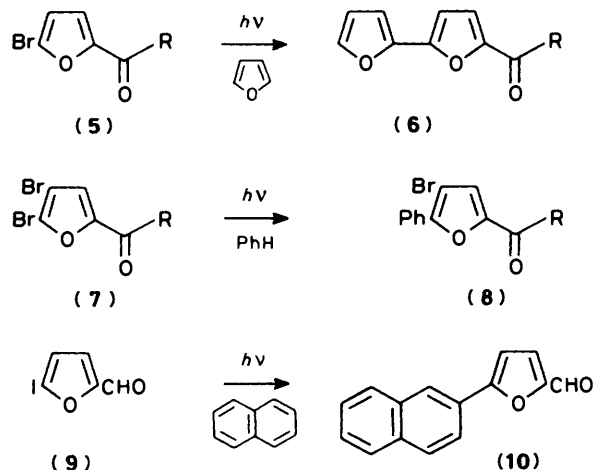
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The irradiation (in benzene solution) of 5-bromo- and 5-iodo-thiophene-2-carbaldehyde or the corresponding methyl ketones furnishes the corresponding 5-phenyl derivatives. The same reactivity for other halogenothiophenes is reported: 3,5-dibromothiophene-2-carbaldehyde furnishes the 3-bromo-5-phenyl-2-thienyl derivative while the corresponding di-iodo compound yields 3,5-diphenylthiophene-2-carbaldehyde. In contrast, 5-acetyl-2,3-di-iodothiophene furnishes only the photosubstitution product at C-5. Generally the iodine-containing compounds are more reactive and more stable under the reaction conditions than ones bearing bromine, in agreement with previous reports on the corresponding furan photochemistry.

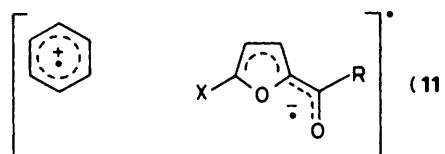
The photochemical synthesis of arylthiophenes (2) and (4) from the corresponding halogenothiophenes (1) and (3) in aromatic solutions was described 20 years ago.¹⁻⁴ The conversion



(1) \longrightarrow (2) probably occurs *via* the formation of the corresponding thienyl radical by homolytic cleavage of the C-I bond. This transformation has not been widely used in organic synthesis.⁵ For this reaction, we observe lower yields than for alternative methods [*i.e.* the reaction of phenylmagnesium bromide with iodide (1) in the presence of $\text{NiCl}_2(\text{dppf})$]. Furthermore, since 2-arylthiophenes (2) undergo a photo-rearrangement on prolonged irradiation, this method should be used with caution.⁷ Finally, no data are available in the literature about the possible extension of this photochemical procedure to halogenothiophenes different from those reported above.



Recently we have reported a new synthetic methodology that furnishes aryl-substituted furancarbaldehydes or ketones (6), (8), or (10) in good yields from the corresponding halogen derivatives. (5), (7), or (9).⁸⁻¹⁰

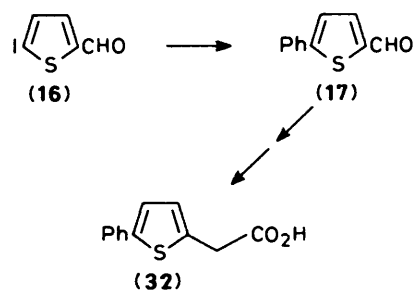


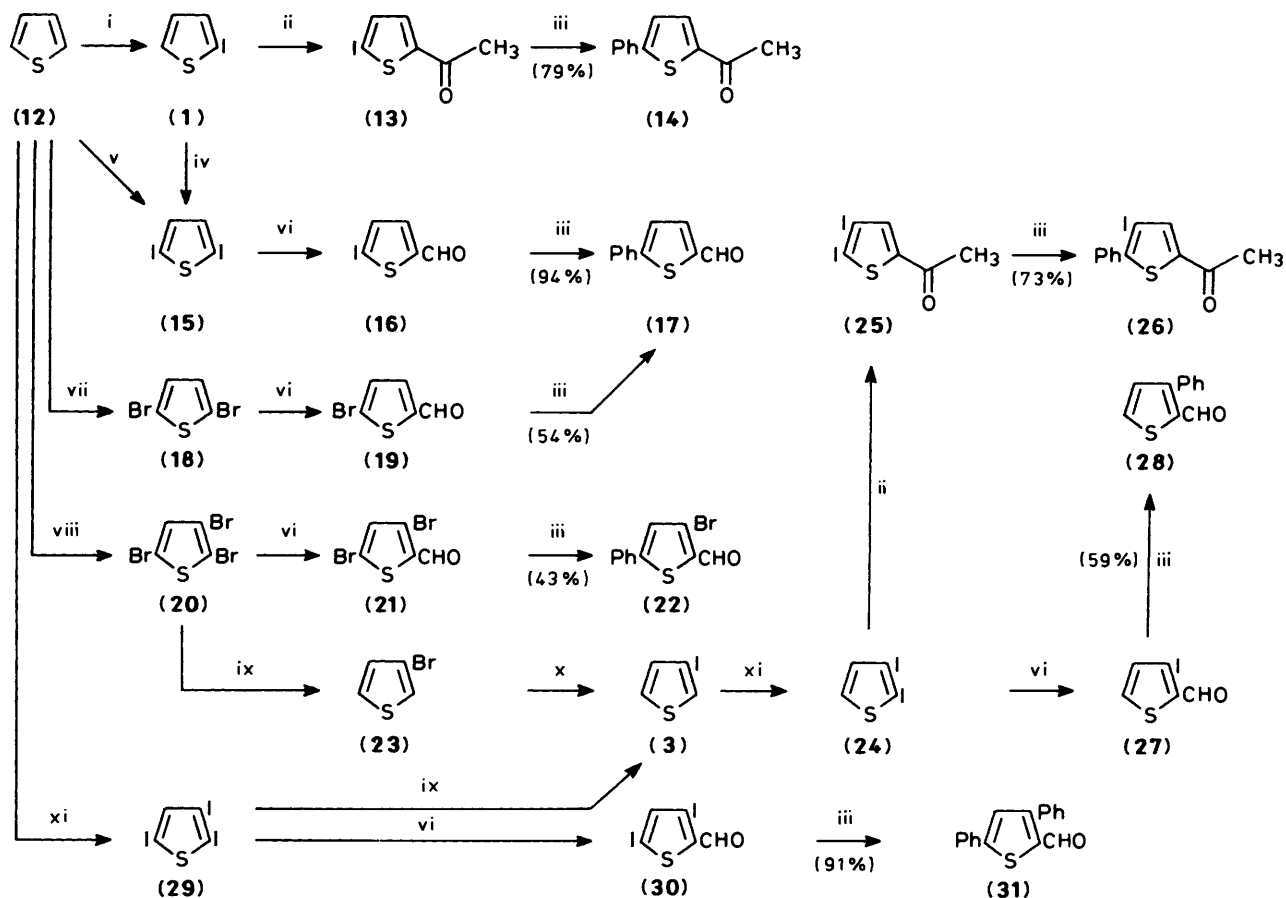
In this case our data are in agreement with the formation of a transient exciplex of type (11).¹¹

In this paper we report our results on the extension of the conversion of type (5) \longrightarrow (6) to thiophene derivatives. In this case, the possible formation of an exciplex of type (11) could not be excluded, since the chemical or photochemical generation of a radical-anion of compounds such as thiophene-2-carbaldehyde is a simple and well known process.^{12,13}

We have prepared some thienyl derivatives (Scheme): these compounds were submitted to irradiation in benzene solution. As expected, the substitution reaction occurs giving high yields of the corresponding aryl derivatives. All the proposed structures of the products were confirmed by their ¹³C n.m.r. data.

From the synthetic point of view, this method constitutes a useful methodology for the preparation of unknown or pharmacologically useful compounds; for example, the anti-inflammatory activity of the acid (32) has been described,¹⁴ and it can be prepared from 5-phenylthiophene-2-carbaldehyde (17) through a known procedure.¹⁴





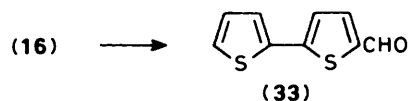
Scheme. Reagents and conditions: i, I_2 , HgO; ii, Ac_2O , H_3PO_4 ; iii, *hv*, PhH; iv, 18-crown-6, $O=P(NMe_2)_3$; v, I_2 , HNO_3 ; vi, BuLi, DMF; vii, Br_2 , AcOH; viii, Br_2 , $CHCl_3$; ix, Zn, AcOH; x, BuLi, I_2 ; xi, I_2 , HIO_3

Iodothieryl derivatives have been shown to be more useful starting material in the photochemical conversion than the bromo derivatives. First, when we use iodothieryl derivatives, the reactions occur under neutral conditions (we observe iodine formation instead of HI); this allows us to extend this methodology to protic-acid-sensitive substrates as well. In addition, iodine-substituted thienyl derivatives can be used in more concentrated solutions without substantial yield decreases and with an important saving of solvent. In contrast, with bromothieryl derivatives, the reaction conditions (see Experimental section) arise from the constraints that (a) the system reaches a photostationary equilibrium which can shift towards the products only with very dilute solutions; (b) we cannot increase the irradiation time because of the observed extensive substrate decomposition under prolonged irradiation (clearly, bromine-containing thiophenes exhibit a high instability under the reaction conditions). This is the most important limit of this procedure when we use bromothieryl compounds. Finally, the iodine-containing compounds (13), (16), (25), (27), and (30) are more reactive than the ones bearing bromine (19) and (21); these results agree with the observed trend in the furan derivatives.

The reaction exhibits an interesting regioselectivity. While 3,5-di-iodothieryl derivative (30) furnishes the corresponding 3,5-diphenylthiophene-2-carbaldehyde (31), 4,5-di-iodothieryl compound (25) gives only the substitution product at C-5, compound (26). Furthermore, the lower reactivity of bromo derivatives in comparison with substrates bearing iodine allows us to observe an interesting increase of regioselectivity: a compound with two bromine atoms, 3,5-dibromothiophene-2-

carbaldehyde (21) furnishes only the arylation product at C-5, compound (22).

Most of the results described above are in agreement with the photochemical behaviour reported in the furan compounds and with the proposed mechanism: in particular, we note that thienyl derivatives are more stable under the reaction conditions than are the corresponding furan derivatives. For example, when 5-iodofuran-2-carbaldehyde (9) reacts with thiophene under irradiation we observe substantial decomposition of the substrate, while the same reaction on 5-iodothiophene-2-carbaldehyde (16) leads to the product (33) in 70% yield.

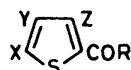


In conclusion, this methodology allows us to obtain both compounds available with difficulty [(14), (28), and (31)] and new compounds [(22) and (26)] with a very simple procedure. Studies on the synthetic applications of our method are in progress.

Experimental

M.p.s were obtained with a Kofler block and are uncorrected. 1H N.m.r. spectra were recorded with a Varian EM-360 spectrometer, using CCl_4 or $CDCl_3$ as solvent with Me_4Si as internal standard. ^{13}C N.m.r. spectra were recorded at 20 MHz

Table. Photochemical behaviour of thiophenes



Entry	Substrate	X	Y	Z	R	Product	X	Y	Z	Z	R	Yield (%) ^a
1	(13)	I	H	H	CH ₃	(14)	Ph	H	H	H	CH ₃	79
2	(16)	I	H	H	H	(17)	Ph	H	H	H	H	94
3	(19)	Br	H	H	H	(17)	Ph	H	H	H	H	54
4	(21)	Br	H	Br	H	(22)	Ph	H	H	Br	H	43
5	(25)	I	I	H	CH ₃	(26)	Ph	I	H	H	CH ₃	73
6	(27)	H	H	I	H	(28)	H	H	H	Ph	H	59
7	(30)	I	H	I	H	(31)	Ph	H	H	Ph	H	91

with a Varian CFT-20 Fourier transform spectrometer, for solutions in CDCl₃. Chemical shifts are given in p.p.m. from internal Me₄Si. I.r. spectra were obtained on Perkin-Elmer 257 and 457 spectrometers. Mass spectra were obtained on a AEI MS-12 instrument at 70 eV, by using direct insertion at a source temperature of 150 °C. U.v. spectra were recorded with a Varian DMS-90 spectrophotometer. Commercial Merck silica gel was used for column chromatography. Carlo Erba precoated silica gel plates were used in t.l.c.

Starting Materials.—2-Iodothiophene (1) was prepared from thiophene by reaction with I₂ and HgO.¹⁵ The product was converted into 2-acetyl-5-iodothiophene (13) by reaction with Ac₂O in the presence of H₃PO₄.¹⁶ 2,5-Di-iodothiophene (15) was obtained from 2-iodothiophene (1) through a disproportionation in the presence of 18-crown-6¹⁷ or by reaction of thiophene (12) with iodine and HNO₃.¹⁸ Di-iodide (15) was converted into 5-iodothiophene-2-carbaldehyde (16) by reaction with BuLi and dimethylformamide (DMF).¹⁹ Similarly, 5-bromothiophene-2-carbaldehyde (19) was prepared from 2,5-dibromothiophene (18). The latter compound was obtained *via* a reaction between thiophene and bromine in the presence of AcOH.²⁰ The synthetic methodology for 3,5-dibromo- (21) and 3,5-di-iodothiophene-2-carbaldehyde (30) involves metalation of 2,3,5-tribromo- (20) and 2,3,5-tri-iodothiophene (29) respectively with BuLi, followed by reaction with DMF.¹⁹ The tribromide was prepared by reaction of thiophene with bromine in CHCl₃.^{21,22} The tri-iodide by reaction of the same substrate with iodine and iodic acid.²³ 2,3,5-Tribromothiophene (20) was also the substrate for the preparation of 3-bromothiophene (23) (by reaction with zinc in AcOH²²) which can in turn be converted into 3-iodothiophene (3) by metalation with BuLi and subsequent reaction with iodine.²⁴ However, 3-iodothiophene can also be prepared by reduction of tri-iodide (29) with zinc dust in AcOH.²³ 3-Iodothiophene (3) can be converted into 2,3-di-iodothiophene (24) by halogenation with iodine and iodic acid.²³ Subsequent metalation of di-iodide (24) with BuLi followed by quenching with DMF¹⁹ furnished 3-iodothiophene-2-carbaldehyde (27). On the other hand, Friedel-Crafts acylation of di-iodide (24) with Ac₂O in the presence of H₃PO₄¹⁶ furnished 5-acetyl-2,3-di-iodothiophene (25).

2-Iodothiophene (1). B.p. 73 °C/15 mmHg (lit.,¹⁵ 73 °C/15 mmHg); δ_H 7.07 (2 H, m), and 6.56 (1 H, m); ν_{max}. 1 397, 1 343, 1 335, 1 218, 1 080, 1 043, 948, 840, 820, 736, and 690 cm⁻¹; *m/z* 210.

2-Acetyl-5-iodothiophene (13). M.p. 128–129 °C (lit.,¹⁶ 129 °C); δ_H 7.20 (2 H, s) and 2.06 (3 H, s); ν_{max}. 1 665, 1 400, 1 358, 1 315, 1 268, 959, and 908 cm⁻¹; *m/z* 252.

2,5-Di-iodothiophene (15). M.p. 40–41 °C (lit.,²⁵ 40.5 °C); δ_H 6.78 (2 H, s); ν_{max}. 1 504, 1 391, 1 340, 1 205, 956, and 927 cm⁻¹; *m/z* 336.

5-Iodothiophene-2-carbaldehyde (16). M.p. 47–49 °C (lit.,¹⁹ 49 °C); δ_H 9.60 (1 H, s) and 7.25 (2 H, s); ν_{max}. 2 820, 2 735, 2 718,

1 680, 1 512, 1 410, 1 388, 1 377, 1 318, 1 219, 1 200, 1 051, 952, and 663 cm⁻¹; *m/z* 238 and 237.

2,5-Dibromothiophene (18). B.p. 210–218 °C (lit.,²⁶ 210.5–211 °C); δ_H 6.67 (2 H, s); ν_{max}. 1 518, 1 410, 1 202, 982, 948, 860, and 782 cm⁻¹; *m/z* 212, 210, and 208.

5-Bromothiophene-2-carbaldehyde (19). B.p. 138–140 °C/30 mmHg (lit.,²⁷ 80–83 °C/2 mmHg); δ_H 9.83 (1 H, s), 7.58 (1 H, d, *J* 4 Hz), and 7.20 (1 H, d, *J* 4 Hz); ν_{max}. 2 818, 2 740, 2 720, 1 668, 1 523, 1 415, 1 391, 1 377, 1 322, 1 303, 1 220, 1 201, 1 185, 1 055, 977, 802, 755, 749, and 663 cm⁻¹; *m/z* 160, 159, 158, and 157.

2,3,5-Tribromothiophene (20). B.p. 136–138 °C/20 mmHg (lit.,²² 123–124 °C/9 mmHg); δ_H 6.72 (1 H, s); ν_{max}. 1 504, 1 411, 1 298, 1 130, 992, 810, 784, and 760 cm⁻¹; *m/z* 292, 290, 288, and 286.

3,5-Dibromothiophene-2-carbaldehyde (21). M.p. 46–47 °C (lit.,²⁸ 48 °C); δ_H 9.68 (1 H, s) and 7.01 (1 H, s); ν_{max}. 2 822, 2 735, 1 673, 1 501, 1 417, 1 360, 1 310, 1 194, 1 140, 988, 689, and 668 cm⁻¹; *m/z* 240, 239, 238, 237, 236, and 235.

3-Bromothiophene (23). B.p. 158–160 °C (lit.,²² 159–160 °C); ν_{max}. 1 492, 1 442, 1 400, 1 352, 1 194, 1 086, 880, 845, 798, 760, and 675 cm⁻¹ (identical with reported spectrum²⁹).

3-Iodothiophene (3). B.p. 64–68 °C/10 mmHg (lit.,²³ 66–68 °C/9 mmHg); δ_H 7.18 (1 H, m) and 6.97 (2 H, m); ν_{max}. 1 482, 1 391, 1 352, 1 338, 1 194, 1 080, 870, 852, 785, 760, and 678 cm⁻¹; *m/z* 210.

2,3-Di-iodothiophene (24). B.p. 131–134 °C/10 mmHg (lit.,²³ 133–135 °C/10 mmHg); δ_H 7.12 (1 H, d, *J* 5 Hz) and 6.64 (1 H, d, *J* 5 Hz); ν_{max}. 1 479, 1 374, 1 328, 1 270, 1 132, 950, 848, 780, 760, and 700 cm⁻¹; *m/z* 336.

5-Acetyl-2,3-di-iodothiophene (25). M.p. 123–124 °C (Found: C, 19.2; H, 1.1. C₆H₄I₂OS requires C, 19.07; H, 1.07%); δ_H 7.33 (1 H, s) and 2.48 (3 H, s); ν_{max}. 1 670, 1 467, 1 372, and 1 263 cm⁻¹; *m/z* 378.

3-Iodothiophene-2-carbaldehyde (27). M.p. 79–80 °C (lit.,¹⁹ 80 °C); δ_H 9.67 (1 H, d, *J* 1.5 Hz), 7.56 (1 H, dd, *J*₁ 5 Hz, *J*₂ 1.5 Hz), and 7.13 (1 H, d, *J* 5 Hz); ν_{max}. 2 733, 1 686, 1 670, 1 490, 1 410, 1 367, 1 340, 1 262, 1 202, 1 155, 878, and 660 cm⁻¹; *m/z* 238 and 237.

2,3,5-Tri-iodothiophene (29). M.p. 83–85 °C (lit.,²³ 82–85 °C); δ_H[(CD₃)₂SO] 7.16 (1 H, s); *m/z* 462.

3,5-Di-iodothiophene-2-carbaldehyde (30). M.p. 103–104 °C (lit.,¹⁹ 104 °C); δ_H 9.50 (1 H, s) and 7.31 (1 H, s); ν_{max}. 1 668, 1 482, 1 402, 1 358, 1 292, and 960 cm⁻¹; *m/z* 364.

Photochemical Synthesis of Phenylthiophene Derivatives.—**General procedure for compounds containing bromine.** Thienyl derivatives (19) and (21) (300 mg) were each dissolved in benzene (300 ml) and the solutions were outgassed with N₂ for 1 h. Each mixture was then irradiated in an immersion apparatus with a 500 W high-pressure mercury arc (Helios-Italquartz) surrounded by a quartz water-jacket. After 2 h each mixture was dissolved in Et₂O and washed with brine. The neutral ethereal phase was dried (Na₂SO₄). Removal of the

solvent yielded a crude product which was chromatographed on SiO₂. Elution with CHCl₃-n-hexane (3:2) gave the pure product (Table).

5-Phenylthiophene-2-carbaldehyde (17). M.p. 92—93 °C (lit.,³⁰ 93—93.5 °C) (Found: C, 70.2; H, 4.2. Calc. for C₁₁H₈OS: C, 70.19; H, 4.28%); δ_H 9.92 (1 H, s) and 7.6 (7 H, m); δ_C 181.7 (d, CHO), 154.8 (s, C-5), 142.5 (s, C-2), 137.4 (d, C-3), and 127.8 (d, C-4); ν_{max}. 1 660, 1 449, 1 438, 1 381, 1 348, 1 107, and 1 052 cm⁻¹; m/z 188 (71%), 187 (51), 177 (86), 175 (100), 131 (30), 115 (30), and 73 (21).

3-Bromo-5-phenylthiophene-2-carbaldehyde (22). M.p. 113—114 °C (Found: C, 49.4; H, 2.5. C₁₁H₇BrOS requires C, 49.46; H, 2.64%); δ_H 9.80 (1 H, s), 7.34 (5 H, m), and 7.15 (1 H, s); δ_C 182.6 (d, CHO), 153.4 (s, C-5), 135.5 (s, C-2), 126.2 (d, C-4), and 120.8 (s, C-3); ν_{max}. 1 660, 1 485, 1 433, 1 360, 1 328, 1 146, 1 107, 1 069, 963, 906, and 838 cm⁻¹; m/z 269 (100%), 268 (88), 267 (98), 266 (77), 159 (50), 116 (32), and 115 (21).

General procedure for compounds containing iodine. Thieryl derivatives (13), (16), (25), (27), and (30) (2 g) were dissolved in benzene (300 ml) and the solutions were outgassed with N₂ for 1 h. Each mixture was then irradiated in an immersion apparatus with a 500 W high-pressure mercury arc (Helios-Italquartz) surrounded by a quartz water-jacket. After 1 h each mixture was dissolved in Et₂O and washed successively with 0.1M Na₂S₂O₃ and then with brine. The ethereal phase was dried (Na₂SO₄). Removal of the solvent yielded a crude product which was chromatographed on SiO₂. Elution with CHCl₃-n-hexane (3:2) gave the pure products (Table).

2-Acetyl-5-phenylthiophene (14). M.p. 113—115 °C (lit.,³¹ 115 °C) (Found: C, 71.35; H, 4.9. Calc. for C₁₂H₁₀OS: C, 71.26; H, 4.98%); δ_H 7.4 (7 H, m) and 2.43 (3 H, s); δ_C 190.4 (s, CO), 152.8 (s, C-5), 143.2 (s, C-2), 133.4 (d, C-3), 126.3 (d, C-4), and 26.5 (q, CH₃); ν_{max}. 1 658, 1 439, 1 360, 1 278, and 1 077 cm⁻¹; m/z 202 (M⁺).

5-Acetyl-3-iodo-2-phenylthiophene (26). Viscous oil (Found: C, 43.8; H, 2.8. C₁₂H₉IOS requires C, 43.92; H, 2.76%); δ_H 7.50 (1 H, s), 7.32 (5 H, m), and 2.47 (3 H, s); δ_C 189.6 (s, CO), 151.4 (s, C-5), 144.3 (s, C-2), 128.7 (d, C-3), 92.8 (s, C-4), and 26.5 (q, CH₃); ν_{max}. 1 675, 1 428, 1 358, and 1 265 cm⁻¹; m/z 329 (63%), 314 (51), 253 (19), 238 (22), 159 (32), 114 (17), 85 (54), and 83 (100).

3-Phenylthiophene-2-carbaldehyde (28). M.p. 35—36 °C (lit.,³² 36.0—36.5 °C) (Found: C, 70.25; H, 4.4. Calc. for C₁₁H₈OS: C, 70.19; H, 4.28%); δ_H 9.60 (1 H, d, J 1.5 Hz), 7.52 (1 H, dd, J₁ 5 Hz, J₂ 1.5 Hz), 7.23 (5 H, m), and 6.98 (1 H, d, J 5 Hz); δ_C 184.1 (d, CHO), 151.4 (s, C-3), 138.6 (s, C-2), 134.0 (d, C-5), and 130.6 (d, C-4); ν_{max}. 1 672, 1 487, 1 448, 1 419, 1 382, 1 361, 1 264, 1 195, 900, 699, 673, and 649 cm⁻¹; m/z 188 (M⁺).

3,5-Diphenylthiophene-2-carbaldehyde (31). M.p. 98—99 °C (lit.,³³ 98—99 °C) (Found: C, 77.2; H, 4.5. Calc. for C₁₇H₁₂OS: C, 77.24; H, 4.58%); δ_H 9.67 (1 H, s), 7.5 (2 H, m), 7.33 (8 H, m), and 7.22 (1 H, s); δ_C 183.8 (d, CHO), 152.6 (s, C-5), 152.2 (s, C-3), 137.2 (s, C-2), and 126.4 (d, C-4); ν_{max}. 1 662, 1 488, 1 454, 1 435, 1 382, 1 367, 1 202, and 700 cm⁻¹; m/z 264 and 263.

5-(2-Thienyl)thiophene-2-carbaldehyde (33). In this case the photochemical reaction was carried out in thiophene (300 ml); the product had m.p. 57—58 °C (lit.,³⁴ 59 °C) (Found: C, 55.6; H, 3.1. Calc. for C₉H₆OS₂: C, 55.64; H, 3.11%); δ_H 9.57 (1 H, s),

7.45 (1 H, d, J 4 Hz), and 7.0 (4 H, m); ν_{max}. 1 673, 1 507, 1 452, 1 227, 1 200, 1 055, 841, and 698 cm⁻¹; m/z 194 (M⁺).

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