New Thiophene Derivatives as Potential Materials for Non Linear Optics

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Dedicated to Professor P. Cagniant on his eightieth birthday.

A method of synthesis of unsymmetrical 2,5-diarylthiophenes is described using β-chloroacroleins, prepared from acetophenones, and their condensation with sodium sulfide and various benzyl bromides.

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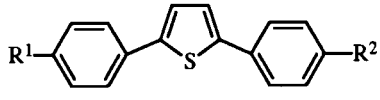
A number of papers dealing with non linear optical material have been published in recent years [1-2]. Introduction of the thiophene nucleus into these compounds has been shown to enhance the non-linear optical properties [3].

We present here the synthesis of a number of thiophene derivatives which may show non-linear optical properties.

The design of the derivatives is based on the Donor-Transmitter-Acceptor moiety and have the following general structure.



Compound	R^1	R^2	Yield (%)	Mp (°C)
5	H	H	35	154 (MeOH) [10]
6	CH_3	H	38	158 (MeOH)
7	OCH_3	H	45	165 (MeOH) [10]
8	F	H	39	164 (MeOH)
9	Cl	H	45	181 (MeOH)
10	Br	H	51	190 (MeOH)
11	$N(CH_3)_2$	H	34	176 (MeOH)
12	H	CO_2CH_3	39	210 (MeOH)
13	CH_3	CO_2CH_3	41	190 (EtOH)
14	OCH_3	CO_2CH_3	44	225 (EtOH)
15	F	CO_2CH_3	40	148 (MeOH)
16	Cl	CO_2CH_3	44	208 (MeOH)
17	Br	CO_2CH_3	49	226 (MeCN)
18	$N(CH_3)_2$	CO_2CH_3	37	216 (MeCN)
19	H	SO_2CH_3	40	222 (MeOH)
20	CH_3	SO_2CH_3	43	262 (EtOH)
21	OCH_3	SO_2CH_3	51	96 (iPrOH)
22	F	SO_2CH_3	43	155 (MeCN)
23	Cl	SO_2CH_3	49	150 (MeOH)
24	Br	SO_2CH_3	53	202 (EtOH)
25	$N(CH_3)_2$	SO_2CH_3	46	195 (iPrOH)
26	H	CN	40	158 (CCl_4)
27	CH_3	CN	46	194 (MeOH)
28	OCH_3	CN	49	158 (MeCN)
29	F	CN	45	162 (MeOH)
30	Cl	CN	51	80 (MeCN)
31	Br	CN	55	222 (MeCN)
32	$N(CH_3)_2$	CN	42	138 (MeOH)
33	H	NO_2	51	137 (MeOH)
34	CH_3	NO_2	53	160 (iPrOH)
35	OCH_3	NO_2	52	154 (EtOH)
36	F	NO_2	50	159 (EtOH)
37	Cl	NO_2	55	168 (EtOH)
38	Br	NO_2	55	134 (AcOEt)
39	$N(CH_3)_2$	NO_2	54	275 (MeOH)

Construction of the desired system cannot be accomplished by electrophilic substitution of 2,5-diphenylthiophene [4-6]. However the synthesis could use a double Heck arylation starting from thiophene. In this case, the work is tedious, requiring the use of often sensitive organometallics (lithiation, stannylation, boronation...). It is also known that the Heck arylation does not work very well when electron-donating groups are present on the aryl nucleus [7].

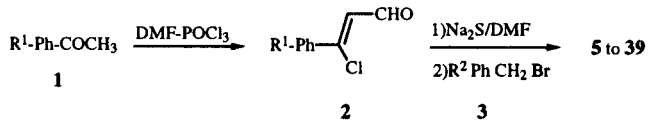
The only 2,5-diarylthiophenes described, in general symmetrical, have been prepared by reaction of the corresponding 1,4-diketones with phosphorus pentasulfide and hydrogen sulfide [8-9], the Lawesson reagent [10] or other sulfur transfering systems [11-12].

We propose a method based on an "one pot synthesis" from β-chloroacrolein derivatives as shown in Scheme 1.

β-Chloroacroleins are easily accessible from the substituted acetophenones **1**, commercially available, by the Vilsmeier-Haack-Arnold reaction [13-14].

The β-chloroacroleins are obtained in good yields (Table 1). The second step is a one-pot synthesis from the β-chloroacroleins **2** to the desired arylthiophenes.

Scheme 1



1 2 3

Compound 2	R^1	Compound 3	R^2
a	H	a	CO_2CH_3
b	CH_3	b	SO_2CH_3
c	OCH_3	c	CN
d	F	d	NO_2
e	Cl		
f	Br		
g	$N(CH_3)_2$		

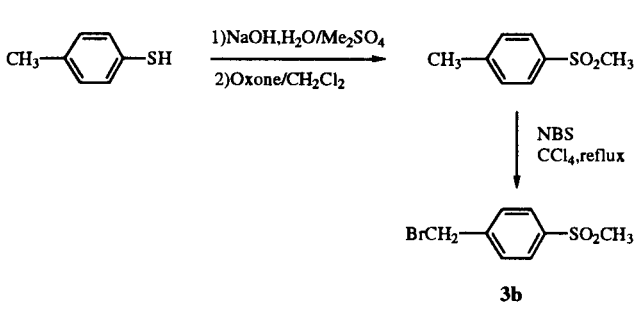
In the first step, sodium sulfide is allowed to react with compounds **2**, followed by condensation with the corresponding benzyl bromides **3**. Choosing in the second step benzyl bromide with an electron withdrawing group in the *para* position allows a direct cyclization to the thiophene by addition of a base, generally sodium methoxide.

In some cases R^2 = nitro or cyano, thus addition of a base is not necessary, the acidity of the methylene group being sufficiently high.

The benzyl bromides are not all commercially available. They can be prepared by NBS bromination of the corresponding para-substituted toluene. In the case of R^2 = methylsulfonyl, the corresponding bromide is prepared as shown in Scheme 2.

The synthesis of the unsubstituted compound **5**, used as a reference in an ongoing uv study, is made, because cyclisation in the case of benzyl bromide does not work very well, as presented in Scheme 3.

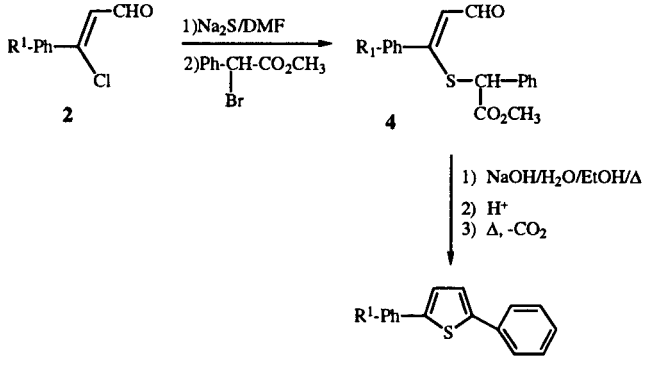
Scheme 2



3b

Condensation of β-chloroacroleines **2** with sodium sulfide and methyl (α-bromo-α-phenyl)acetate, leads to the derivatives **4**, where the acidity of the methyne allows the cyclzation, completed by hydrolysis and decarboxylation.

Scheme 3



2 4

5, 6, 7, 8, 9, 10, 11

Table I

β-Chloroacroleins **2**

Compound	Mp°C, bp °C (Torr)	Yield (%)	Molecular Formula	Analysis Calcd./Found C	H	N	^{1}H NMR ($CDCl_3$)
2a	140 (20) (128/15) [15]	90	C_9H_7ClO	64.80 64.60	4.20 4.60		6.55 (d, 1H), 7.2 (m, 2H, Ar-H), 7.4 (m, 3H, Ar-H) 10.15 (d, 1H)
2b	153/15 [16]	85	$C_{10}H_9ClO$	66.11 65.86	5.50 5.43		2.3 (s, 3H, CH_3), 6.65 (d, 1H), 6.8 (d, 2H, J = 4.1 Hz), 7.3 (d, 2H, J = 4.1 Hz), 10.1 (d, 1H)
2c	57[17]	90	$C_{10}H_9ClO_2$	61.06 60.74	4.58 4.36		3.8 (s, 3H, OCH_3), 6.55 (d, 1H), 7.0 (d, 2H, J = 5.8 Hz), 7.8 (d, 2H, J = 5.8 Hz), 10.25 (d, 1H)
2d	72	70	C_9H_6ClFO	58.53 58.21	3.25 3.03		6.55 (d, 1H), 7.4 (m, 4H, Ar-H), 10.15 (d, 1H)
2e	86 (83 [17])	85	$C_9H_6Cl_2O$	53.46 53.41	2.50 2.45		6.65 (d, 1H), 7.4 (d, 2H, J = 8.4 Hz), 7.7(d, 2H, J = 8.4 Hz), 10.1 (d, 1H)
2f	79 (80 [17])	80	C_9H_6BrClO	43.99 44.26	2.44 2.57		6.6 (d, 1H), 7.6 (d, 2H, J = 4.1 Hz), 7.7 (d, 2H, J = 4.1 Hz), 10.1 (d,1H)
2g	114	80	$C_{11}H_{12}ClNO$	62.70 63.01	6.17 6.15	6.65 6.61	3.0 (s, 6H), 6.55 (d, 1H), 6.7 (d, 2H, J = 5.8 Hz), 7.7 (d, 2H, J = 5.8 Hz), 10.1 (d, 1H)

Table II

Substituted 2,5-Diphenylthiophene

Compound	Molecular Formula	Analysis Calcd./Found C	H	N	^{1}H NMR (DMSO)	UV λ max (nm)	ε
5	$C_{16}H_{12}S$	81.35 80.96	5.08 5.10		7.4 (m, 6H, Ar-H), 7.55 (s, 2H, Ar-H), 7.7 (m, 4H, Ar-H), 7.7 (m, 4H, Ar-H)	323	27000
6	$C_{17}H_{14}S$	81.60 81.72	5.60 5.66		2.35 (s, 3H, CH_3), 7.25 (d, 2H, J = 6.9 Hz), 7.3 (d, 1H, J = 6.3 Hz), 7.4 (d, 1H, J = 6.3 Hz), 7.5 (m, 2H, Ar-H), 7.6 (m, 2H, Ar-H), 7.7 (d, 2H, J = 6.9 Hz)	326	29100
7	$C_{17}H_{14}OS$	77.69 78.02	5.26 4.87		4.4 (s, 3H, OCH_3), 6.95 (d, 2H, J = 7.7 Hz), 7.3 (m, 3H, Ar-H), 7.4 (d, 1H, J = 3.5 Hz), 7.5 (d, 1H, J = 3.5), 7.6 (m, 2H, Ar-H), 7.75 (d, 2H, J = 7.7 Hz)	320	15000
8	$C_{16}H_{11}FS$	75.88 75.51	4.34 4.27		7.35 (m, 5H, Ar-H), 7.5 (d, 1H, J = 2.8 Hz), 7.6 (d, 1H, J = 2.8 Hz), 7.7 (m, 4H, Ar-H)	322	20600
9	$C_{16}H_{11}ClS$	70.97 71.20	5.26 4.91		7.4 (m, 5H, Ar-H), 7.55 (d, 1H, J = 2.8 Hz), 7.6 (d, 1H, J = 2.8 Hz), 7.7 (d, 2H, J = 5.6 Hz), 7.75 (d, 2H, J = 5.6 Hz)	327	34900
10	$C_{18}H_{17}BrS$	60.95 60.66	3.49 3.43		7.4 (m, 1H, Ar-H), 7.5 (d, 1H, J = 4.2 Hz), 7.55 (d, 1H, J = 4.2 Hz), 7.6 (d, 2H, J = 7.3 Hz), 7.65 (m, 2H, Ar-H), 7.7 (d, 2H, J = 7.3 Hz)	315	19300
11	$C_{18}H_{17}NS$	78.35 77.92	5.84 5.83	4.81 4.68	2.9 (s, 6H, $N(CH_3)_2$), 6.75 (d, 2H, J = 8.4 Hz), 7.3 (m, 2H, Ar-H), 7.35 (d, 1H, J = 2.8 Hz), 7.4 (d, 1H, J = 2.8 Hz), 7.5 (m, 3H, Ar-H), 7.7 (d, 2H, J = 8.4 Hz)	356	14600
12	$C_{18}H_{14}O_2S$	73.46 73.42	4.76 4.87		3.9 (s, 3H, CH_3), 7.35 (m, 3H, Ar-H), 7.6 (d, 1H, J = 3.5 Hz), 7.7 (m, 2H, Ar-H), 7.75 (d, 1H, J = 3.5 Hz), 7.85 (d, 2H, J = 7.7 Hz), 8.0 (d, 2H, J = 7.7 Hz)	346	9500
13	$C_{19}H_{16}O_2S$	74.53 74.18	5.59 4.31		1.35 (t, 3H, CH_2CH_3), 2.4 (s, 3H, CH_3), 4.35 (q, 2H, CH_2CH_3), 7.25 (d, 2H, J = 7 Hz), 7.55 (d, 1H, J = 3.5 Hz), 7.6 (d, 2H, J = 7 Hz), 7.65 (d, 1H, J = 3.5 Hz), 7.8 (d, 2H, J = 7.7 Hz), 8.0 (d, 2H, J = 7.7 Hz)	349	32200
14	$C_{19}H_{16}O_2S$	66.66 66.35	4.93 4.55		3.75 (s, 3H, OCH_3), 3.85 (s, 3H, CH_3), 6.95 (d, 2H, J = 7.7 Hz), 7.3 (d, 1H, J = 3.5 Hz), 7.65 (d, 1H, J = 3.5 Hz), 7.8 (d, 2H, J = 7.7 Hz), 7.85 (d, 2H, J = 7.7 Hz), 8.0 (d, 2H, J = 7.7 Hz)	355	22100
15	$C_{18}H_{13}FO_2S$	69.23 69.01	4.16 4.07		3.9 (s, 3H, CH_3), 7.3 (m, 2H, Ar-H), 7.6 (m, 2H, Ar-H), 7.7 (d, 1H, J = 3.5 Hz), 7.75 (d, 1H, J = 3.5 Hz), 7.9 (d, 2H, J = 7.7 Hz), 8.0 (d, 2H, J = 7.7 Hz)	340	12100
16	$C_{18}H_{13}ClO_2S$	65.75 65.64	3.95 3.51		3.9 (s, 3H, CH_3), 7.5 (d, 2H, J = 7 Hz), 7.6 (d, 1H, J = 3.5 Hz), 7.65 (d, 1H, J = 3.5 Hz), 7.75 (d, 2H, J = 7 Hz), 7.85 (d, 2H, J = 7.7 Hz), 7.95 (d, 2H, J = 7.7 Hz)	361	34000
17	$C_{18}H_{13}BrO_2S$	57.90 57.54	3.48 3.28		3.9 (s, 3H, CH_3), 7.5 (d, 1H, J = 3.5 Hz), 7.6 (d, 2H, J = 8.4 Hz), 7.6 (d, 2H, J = 8.4 Hz), 7.7 (d, 2H, J = 8.4 Hz), 7.75 (d, 1H, J = 3.5 Hz), 7.8 (d, 2H, J = 7.7 Hz), 8.0 (d, 2H, J = 7.7 Hz)	348	15200
18	$C_{20}H_{19}NO_2S$	71.21 70.97	5.63 5.70	4.15 4.08	3.1 (s, 6H, $N(CH_3)_2$), 3.9 (s, 3H, CH_3), 6.85 (d, 2H, J = 8.4 Hz), 7.5 (d, 1H, J = 3.5 Hz), 7.6 (d, 2H, J = 8.4 Hz), 7.7 (d, 1H, J = 3.5 Hz), 7.8 (d, 2H, J = 7.7 Hz), 7.95 (d, 2H, J = 7.7 Hz)	270	6700
19	$C_{18}H_{14}O_2S_2$	64.96 64.99	4.45 4.18		3.25 (s, 3H, SO_2CH_3), 7.4 (m, 3H, Ar-H), 7.6 (d, 1H, J = 4.2 Hz), 7.65 (m, 2H, Ar-H), 7.75 (d, 1H, J = 4.2 Hz), 7.95 (s, 4H, Ar-H)	341	22700
20	$C_{19}H_{17}O_2S_2$	65.85 66.01	4.87 4.75		2.35 (s, 3H, CH_3), 3.25 (s, 3H, SO_2CH_3), 7.25 (d, 2H, J = 7 Hz), 7.55 (d, 1H, J = 3.5 Hz), 7.6 (d, 2H, J = 7 Hz), 7.75 (d, 1H, J = 3.5 Hz), 7.95 (s, 4H, Ar-H)	346	6700
21	$C_{19}H_{17}O_3S_2$	62.79 62.61	4.65 4.54		3.25 (s, 3H, SO_2CH_3), 4.35 (s, 3H, OCH_3), 7.0 (d, 2H, J = 7.7 Hz), 7.55 (d, 1H, J = 5.6 Hz), 7.65 (d, 1H, J = 5.6 Hz), 7.85 (d, 2H, J = 7.7 Hz), 7.95 (d, 2H, J = 7.7 Hz)	362	12300
22	$C_{18}H_{13}FO_2S_2$	61.44 61.07	3.91 3.82		3.25 (s, 3H, SO_2CH_3), 7.5 (m, 4H, Ar-H), 7.6 (d, 1H, J = 3.5 Hz), 7.75 (d, 1H, J = 3.5 Hz), 7.95 (s, 4H, Ar-H)	342	29300
23	$C_{18}H_{13}ClO_2S_2$	58.62 58.27	3.73 3.89		3.25 (s, 3H, SO_2CH_3), 7.45 (d, 2H, J = 7.7 Hz), 7.65 (d, 1H, J = 4.2 Hz), 7.75 (d, 2H, J = 7.7 Hz), 7.8 (d, 1H, J = 4.2 Hz), 7.95 (s, 4H, Ar-H)	342	21400
24	$C_{18}H_{13}BrO_2S_2$	51.90 51.75	3.30 3.21		3.25 (s, 3H, SO_2CH_3), 7.55 (d, 1H, J = 3.5 Hz), 7.6 (d, 2H, J = 8.4 Hz), 7.65 (d, 2H, J = 8.4 Hz), 7.75 (d, 1H, J = 3.5 Hz), 7.95 (s, 4H, Ar-H)	342	29300
25	$C_{20}H_{19}NO_2S$	63.86 64.09	5.32 5.20	3.92 3.60	2.95 (s, 6H, $N(CH_3)_2$), 3.25 (s, 3H, SO_2CH_3), 6.75 (d, 2H, J = 7.7 Hz), 7.35 (d, 1H, J = 5.5 Hz), 7.7 (d, 1H, J = 3.5 Hz), 7.75 (d, 2H, J = 7.7 Hz), 7.95 (s, 4H, Ar-H)	387	6100
26	$C_{17}H_{11}NS$	78.16 77.81	4.21 4.03	5.36 5.34	7.4 (m, 3H, Ar-H), 7.6 (d, 1H, J = 3.5 Hz), 7.65 (m, 2H, Ar-H), 7.75 (d, 1H, J = 3.5 Hz), 7.9 (s, 4H, Ar-H)	345	27500

Table II (continued)

Compound	Molecular Formula	Analysis Calcd./Found C	H	N	^{1}H NMR (DMSO)	UV λ max (nm)	ε
27	$C_{18}H_{14}NS$	78.54 78.39	4.72 4.93	5.09 5.47	2.35 (s, 3H, CH_3), 7.2 (d, 2H, J = 7.7 Hz), 7.55 (d, 1H, J = 3.5 Hz), 7.6 (d, 1H, J = 7 Hz), 7.7 (d, 1H, J = 3.5 Hz), 7.85 (s, 4H, Ar-H)	350	30900
28	$C_{18}H_{14}NOS$	74.22 73.93	4.46 4.16	4.81 4.91	3.8 (s, 3H, OCH_3), 7.0 (d, 2H, J = 7.7 Hz), 7.45 (d, 1H, J = 3.5 Hz), 7.6 (d, 2H, J = 7.7 Hz), 7.7 (d, 1H, J = 3.5 Hz), 7.85 (s, 4H, Ar-H)	359	21800
29	$C_{17}H_{11}FNS$	73.11 72.86	3.58 3.40	5.01 4.89	7.3 (m, 2H, Ar-H), 7.6 (d, 1H, J = 3.5 Hz), 7.7 (d, 1H, J = 3.5 Hz), 7.75 (m, 2H, Ar-H), 7.9 (s, 4H, Ar-H)	345	35400
30	$C_{17}H_{11}ClNS$	69.03 68.74	3.38 3.71	4.73 5.04	7.5 (d, 2H, J = 7.7 Hz), 7.6 (d, 1H, J = 3.5 Hz), 7.7 (d, 2H, J = 7.7 Hz), 7.75 (d, 1H, J = 3.5 Hz), 7.9 (s, 4H, Ar-H)	349	15800
31	$C_{17}H_{11}ClNS$	60.00 59.84	2.94 2.91	4.11 4.02	7.55 (d, 1H, J = 3.5 Hz), 7.6 (d, 2H, J = 8.4 Hz), 7.65 (d, 1H, J = 8.4 Hz), 7.75 (d, 1H, J = 3.5 Hz), 7.9 (s, 4H, Ar-H)	350	42500
32	$C_{19}H_{17}N_2S$	75.00 75.32	5.26 5.61	9.21 9.21	2.95 (s, 6H, $N(CH_3)_2$), 6.95 (d, 2H, J = 8.4 Hz), 7.55 (d, 1H, J = 3.5 Hz), 7.6 (d, 2H, J = 8.4 Hz), 7.7 (d, 1H, J = 3.5 Hz), 7.9 (s, 4H, Ar-H)	389	14800
33	$C_{16}H_{11}NO_2S$	68.32 68.01	3.91 3.83	4.98 5.04	7.4 (m, 3H, Ar-H), 7.65 (d, 1H, J = 4.9 Hz), 7.7 (m, 2H, Ar-H), 7.85 (d, 1H, J = 4.9 Hz), 7.95 (d, 2H, J = 8.4 Hz), 8.3 (d, 2H, J = 8.4 Hz)	378	18100
34	$C_{17}H_{14}NO_2S$	69.15 68.76	4.40 4.20	4.74 4.86	2.5 (s, 3H, CH_3), 7.25 (d, 2H, J = 7 Hz), 7.6 (d, 1H, J = 3.5 Hz), 7.65 (d, 2H, J = 7 Hz), 7.75 (d, 1H, J = 3.5 Hz), 7.95 (d, 2H, J = 8.4 Hz), 8.3 (d, 2H, J = 8.4 Hz)	384	25100
35	$C_{17}H_{14}NO_3S$	56.93 56.84	3.63 3.46	3.91 3.71	3.8 (s, 3H, OCH_3), 7.0 (d, 2H, J = 7.7 Hz), 7.5 (d, 1H, J = 3.5 Hz), 7.65 (d, 2H, J = 7.7 Hz), 7.85 (d, 1H, J = 3.5 Hz), 7.95 (d, 2H, J = 8.4 Hz), 8.3 (d, 2H, J = 8.4 Hz)	392	12500
36	$C_{16}H_{10}FNO_2S$	64.21 64.02	3.34 3.31	4.68 4.60	7.55 (m, 4H, Ar-H), 7.6 (d, 1H, J = 3.5 Hz), 7.75 (d, 1H, J = 3.5 Hz), 7.9 (s, 4H, Ar-H)	346	21900
37	$C_{16}H_{10}ClNO_2S$	60.85 61.10	3.16 2.87	4.43 4.86	7.45 (d, 2H, J = 7 Hz), 7.7 (d, 1H, J = 3.5 Hz), 7.75 (d, 2H, J = 7 Hz), 7.85 (d, 1H, J = 3.5 Hz), 7.95 (d, 2H, J = 8.4 Hz), 8.3 (d, 2H, J = 8.4 Hz)	377	26200
38	$C_{16}H_{10}BrNO_2S$	53.33 53.41	2.77 2.60	3.88 3.90	7.5 (d, 1H, J = 3.5 Hz), 7.6 (d, 2H, J = 8.4 Hz), 7.7 (d, 2H, J = 8.4 Hz), 7.75 (d, 1H, J = 3.5 Hz), 7.95 (d, 2H, J = 8.4 Hz), 8.3 (d, 2H, J = 8.4 Hz)	380	5400
39	$C_{18}H_{16}N_2O_2S$	66.66 66.51	4.93 4.91	8.64 8.78	3.05 (s, 6H, $N(CH_3)_2$), 7.2 (d, 2H, J = 7.7 Hz), 7.5 (d, 1H, J = 3.5 Hz), 7.65 (d, 1H, J = 3.5 Hz), 7.7 (d, 2H, J = 7.7 Hz), 7.9 (d, 2H, J = 8.4 Hz), 8.1 (d, 2H, J = 8.4 Hz)	430	1700

All the compounds prepared were characterized by ^{1}H nmr spectroscopy and microanalysis. The results are given in Table II.

EXPERIMENTAL

Melting points were determined on a Kofler bench and are uncorrected. The ^{1}H nmr were recorded with a Bruker 250 MHz spectrometer. Elemental analysis were performed on a Carlo Erba elemental analyser and uv on a Beckman DU 640 spectrometer.

β-Chloroacroleins **2**.

DMF (11 ml) was added to an ice cold solution of phosphoryl chloride (11 ml) and the mixture stirred for 10 minutes. To the Vilsmaier-Haack reagent, ketone **1** (0.1 mole) in 30 ml of DMF was added dropwise and the mixture was stirred 3 hours at 60°. Pouring the reaction mixture into an aqueous sodium acetate solution yielded the β-Chloroacroleins **2** which were filtered or extracted with ether. Purification was accomplished by recrystallization or distillation.

2,5-Diphenylthiophenes **5** to **39**.

Compound **2** (0.1 mole) in 50 ml of DMF was added dropwise to a suspension of sodium sulfide nonahydrate (0.1 mole) in 50 ml of DMF at room temperature. After 2 hours, benzyl bromide **3** (0.1 mole) in DMF was added and the mixture was heated for 3 hours at 50°. Sodium methoxide (0.1 mole) in methanol was added and after 10 minutes the mixture was poured into cold water and acidified. The crude product was isolated by filtration and purified by recrystallization.

Methyl 4-Bromomethylbenzenesulfonate **3b**.

The methyl *p*-toluenesulfonate derivative (0.1 mole) was dissolved in 400 ml of carbon tetrachloride and heated to reflux. NBS (0.1 mole) was then added at such a rate as to maintain the

reflux. After 3 hours, heating was stopped and the cooled mixture filtered. The filtrate was evaporated under reduced pressure and the solid obtained recrystallized.

Methyl 4-Bromomethylbenzenesulfonate **3b** had mp 80°; ^{1}H nmr (deuteriochloroform): δ 3.05 (s, 3H, SO_2CH_3), 4.55 (s, 2H, CH_2Br), 7.6 (d, 2H, Ar-H), 7.95 (d, 2H, Ar-H).

Anal. Calcd. for $C_8H_9O_2SBr$: C, 38.55; H, 4.33. Found: C, 38.44; H, 4.26.

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