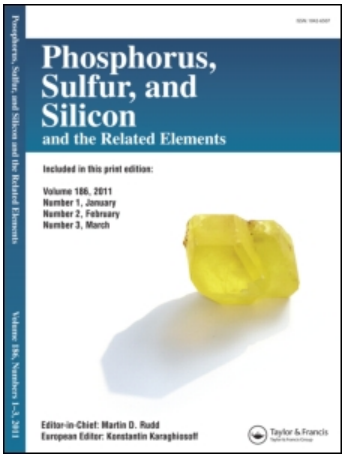

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SYNTHESIS OF NEW 2,5-DIARYL SELENOPHENES

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SYNTHESIS OF NEW 2,5-DIARYL SELENOPHENES

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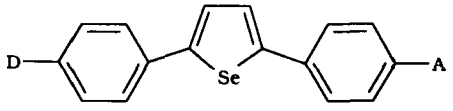
A synthesis of 2,5-parasubstituted diaryl selenophenes is described. β-Aryl-β-chloro acroleins, easily prepared from substituted acetophenones and Vilsmaier-Haack reagent, are condensed with appropriate benzylbromide derivatives to give the title compounds.

Key words: Vilsmaier-Haack, β-aryl-β-chloro acroleins, u.v. spectroscopy, selenophene, 2,5-diaryl selenophenes, non-linear optical material.

INTRODUCTION

As part of our continuing interest in non-linear optical material,[1] we have synthetised various 2,5-diaryl selenophenes. Thiophene is often used in organic conductors[2] and in non-linear optical devices,[3] but only one selenium heterocyclic ring system has been described for this use.

Wudl[4] described 3,4-diamino-2,5-dicyano selenophene as an organic semiconductor. In the Donor-Transmitter-Acceptor model **1** we have chosen (Scheme I), the selenophene ring as a part of the π system transmitting the electronic effects.



1

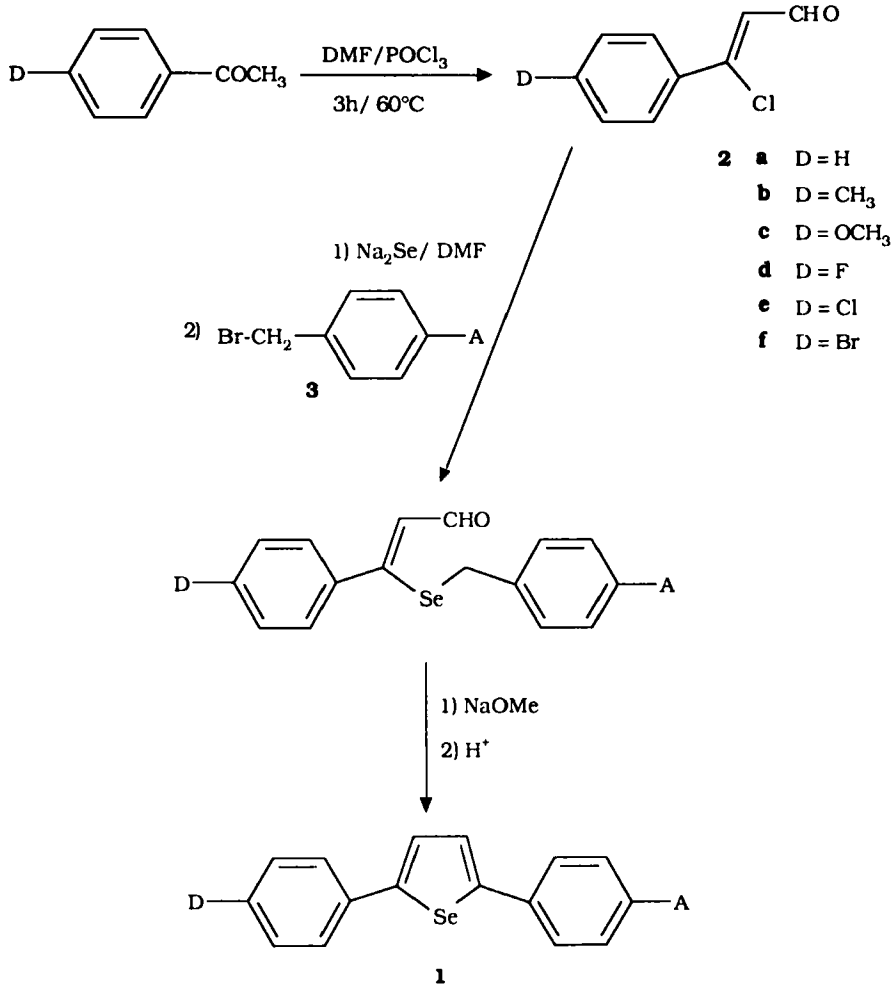
D : **a** = H	**A** : **g** = CO_2Me
b = Me	**h** = SO_2Me
c = MeO	**i** = CN
d = F	**j** = NO_2
e = Cl	
f = Br	

SCHEME I Donor-Transmitter-Acceptor, general structure.

RESULTS AND DISCUSSION

Only a few examples of 2,5-diaryl selenophenes are described, prepared by heating selenium with 2,5-diaryl-1,4-dithiin-1,1,4,4-tetroxides.[5] Substituted selenophenes have been prepared by the general method described in previous work.[6] Using this methodology, we have prepared 21 new diaryl selenophenes. The general method is outlined in Scheme II.

β-Aryl-β-chloro acroleins **2**, prepared in good yields from acetophenones and the Vilsmaier-Haack reagent, are obtained as a mixture of two isomers Z and E but do not have to be separated for the next step. Compounds **2** are listed in Table I. In the second step, compounds **2** are reacted with sodium selenide in DMF and



SCHEME II Preparation of 2,5-diaryl selenophenes **1**.

TABLE I

β-Aryl-β-Chloroacroleins **2**

Compound	Mp °C, bp °C (Torr)	Yield (%)	Molecular Formula	Analysis C (found)	H	N	^{1}H NMR ($CDCl_3$)
2a	140 (20)	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	(128/15)[7] 153/15[8]	85	$C_{10}H_9ClO$	66.11 (65.86	5.50 5.43)		2.3 (s, 3H, $C\underline{H}_3$), 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[9]	90	$C_{10}H_9ClO_2$	61.06 (60.74	4.58 4.36)		3.8 (s, 3H, $OC\underline{H}_3$), 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[9])	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[9])	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)

the appropriate benzylbromides **3**. Cyclisation is achieved with sodium methoxide. The diaryl selenophenes prepared in this way are shown in Tables II and III. Comparison of spectroscopic uv absorption between previously described 2,5-diaryl thiophenes[1] and 2,5-diaryl selenophenes substituted by the same donor and acceptor groups shows generally bathochromic displacement of λ max in the selenophenic series.

Characterisation of the non-linear optical properties is underway.

EXPERIMENTAL

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

β-Aryl-β-chloroacrolein **2**. *General procedure.* 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, acetophenone (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-aryl-β-chloroacroleins **2** which were filtered or extracted with ether. Purification was accomplished by recrystallization or distillation (Table I).

2,5-Diaryl selenophene **1**. *General procedure.* Compound **2** (0.1 mole) in 50 ml of DMF was added dropwise to a suspension of sodium selenide (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 (Table II).

TABLE II

2,5-Diaryl selenophenes **1**

Compound	Molecular Formula	Yield (%)	mp (°C)	analysis C (found)	analysis H (found)	analysis N (found)	RMN ^{1}H (DMSO) J (Hz)
1a, g	$C_{18}H_{14}O_2Se$	26	230 (MeOH)	63.34 (63.28	4.10 3.83)		3.25 (s, 3H, $C\underline{H}_3$), 7.4 (m, 3H, Ar-H), 7.5 (d, 1H, J = 3.6), 7.7 (m, 2H, Ar-H), 7.75 (d, 1H, J = 3.6), 7.9 (d, 2H, J = 7.8), 7.95 (d, 2H, J = 7.8)
1d, g	$C_{18}H_{13}FO_2Se$	29	196 (MeOH)	60.33 (60.08	3.63 3.81)		3.9 (s, 3H, $C\underline{H}_3$), 7.3 (m, 2H, Ar-H), 7.6 (m, 2H, Ar-H), 7.7 (d, 1H, J = 3.5), 7.75 (d, 1H, J = 3.5), 7.9 (d, 2H, J = 7.7), 8.0 (d, 2H, J = 7.7)
1e, g	$C_{18}H_{13}ClO_2Se$	33	204 (MeCN)	57.52 (57.40	3.46 3.62)		3.9 (s, 3H, $C\underline{H}_3$), 7.5 (d, 2H, J = 7), 7.6 (d, 1H, J = 3.5), 7.65 (d, 1H, J = 3.5), 7.75 (d, 2H, J = 7), 7.85 (d, 2H, J = 7.7), 7.95 (d, 2H, J = 7.7)
1a, h	$C_{17}H_{14}O_2SSe$	40	234 (MeCN)	56.09 (55.89	3.87 3.65)		3.25 (s, 3H, $SO_2C\underline{H}_3$), 7.4 (m, 3H, Ar-H), 7.5 (d, 1H, J = 3.5), 7.65 (m, 2H, Ar-H), 7.75 (d, 1H, J = 3.5), 7.90 (d, 2H, J = 7.7), 7.95 (d, 2H, J = 7.7)
1b, h	$C_{18}H_{16}O_2SSe$	40	275 (MeCN)	57.60 (57.41	4.26 4.10)		2.35 (s, 3H, $C\underline{H}_3$), 3.3 (s, 3H, $SO_2C\underline{H}_3$), 7.25 (d, 2H, J = 7.2), 7.5 (d, 1H, J = 3.5), 7.55 (d, 2H, J = 7.2), 7.7 (d, 1H, J = 3.5), 7.9 (d, 2H, J = 7), 7.95 (d, 2H, J = 7)
1c, h	$C_{18}H_{16}O_3SSe$	39	291 (MeCN)	55.24 (55.43	4.09 4.01)		3.25 (s, 3H, $SO_2C\underline{H}_3$), 3.8 (s, 3H, $OC\underline{H}_3$), 7.0 (d, 2H, J = 8.4), 7.1 (d, 1H, J = 3.5), 7.6 (d, 2H, J = 8.4), 7.75 (d, 1H, J = 3.5), 7.85 (d, 2H, J = 7), 7.9 (d, 2H, J = 7)
1d, h	$C_{17}H_{13}FO_2SSe$	36	238 (MeCN)	53.82 (53.64	3.43 3.49)		3.3 (s, 3H, $SO_2C\underline{H}_3$), 7.3 (m, 2H, Ar-H), 7.7 (m, 2H, Ar-H), 7.75 (d, 1H, J = 3.5), 7.85 (d, 2H, J = 7.7), 7.9 (d, 2H, J = 7.7), 7.95 (d, 1H, J = 3.5)
1e, h	$C_{17}H_{13}ClO_2SSe$	49	230 (MeOH)	51.58 (51.33	3.28 3.14)		3.3 (s, 3H, $SO_2C\underline{H}_3$), 7.5 (d, 2H, J = 7.5), 7.7 (d, 2H, J = 7.5), 7.8 (d, 1H, J = 3.6), 7.85 (d, 2H, J = 7.7), 7.95 (d, 2H, J = 7.7), 8.0 (d, 1H, J = 3.5)
1f, h	$C_{17}H_{13}BrO_2SSe$	41	241 (MeCN)	46.36 (46.11	2.95 2.35)		3.3 (s, 3H, $SO_2C\underline{H}_3$), 7.55 (d, 1H, J = 3.5), 7.6 (d, 2H, J = 8.4), 7.65 (d, 2H, J = 8.4), 7.75 (d, 2H, J = 7.7), 7.95 (d, 1H, J = 7.7), 8.0 (d, 2H, J = 7.7)

TABLE II (*Continued*)

Compound	Molecular Formula	Yield (%)	mp (°C)	analysis C (found)	H (found)	N (found)	RMN ^{1}H (DMSO) *J* (Hz)
Ia, i	$C_{17}H_{11}NSe$	33	185 (EtOH)	64.86 (65.03	3.71 3.33	4.72 4.74)	7.4 (m, 3H, Ar-H), 7.6 (m, 2H, Ar-H), 7.7 (d, 1H, *J* = 3.5), 7.8 (d, 2H, *J* = 7.7), 7.85 (d, 2H, *J* = 7.7), 7.9 (d, 1H, *J* = 3.5)
Ib, i	$C_{18}H_{13}NSe$	38	213 (MeOH)	67.28 (67.20	4.03 4.06	4.34 4.37)	2.35 (s, 3H, $C\underline{H}_3$), 7.2 (d, 2H, *J* = 7.7), 7.5 (d, 2H, *J* = 7.7), 7.65 (d, 1H, *J* = 4.2), 7.8 (d, 2H, *J* = 7), 7.85 (d, 2H, *J* = 7), 7.9 (d, 1H, *J* = 3.5)
Ic, i	$C_{18}H_{14}NOSe$	40	158 (MeCN)	64.09 (63.81	3.85 3.66	4.15 4.01)	3.8 (s, 3H, $OC\underline{H}_3$), 6.95 (d, 2H, *J* = 7.7), 7.55 (d, 2H, *J* = 7.7), 7.65 (d, 1H, *J* = 3.5), 7.8 (d, 2H, *J* = 7), 7.85 (d, 2H, *J* = 7), 7.9 (d, 1H, *J* = 3.5)
Id, i	$C_{17}H_{11}FNSe$	29	154 (MeOH)	62.76 (62.81	3.07 3.26	4.30 4.21)	7.25 (m, 2H, Ar-H), 7.6 (d, 1H, *J* = 3.5), 7.8 (d, 2H, *J* = 7), 7.85 (m, 2H, Ar-H), 7.9 (d, 2H, *J* = 7), 7.95 (d, 1H, *J* = 3.5)
Ie, i	$C_{17}H_{11}ClNSe$	28	178 (MeCN)	59.73 (59.98	2.92 2.87	4.09 4.02)	7.45 (d, 2H, *J* = 7.7), 7.65 (d, 2H, *J* = 7.7), 7.75 (d, 1H, *J* = 3.5), 7.85 (d, 2H, *J* = 7), 7.9 (d, 2H, *J* = 7), 7.95 (d, 1H, *J* = 3.5)
If, i	$C_{17}H_{11}BrNSe$	41	173 (MeCN)	52.71 (52.99	2.58 2.41	3.61 3.95)	7.55 (s, 4H, Ar-H), 7.65 (d, 1H, *J* = 3.5), 7.75 (d, 2H, *J* = 7), 7.85 (d, 2H, *J* = 7), 7.9 (d, 1H, *J* = 3.5)
Ia, j	$C_{16}H_{11}NO_2Se$	39	210 (MeCN)	58.53 (58.61	3.35 3.52	4.26 5.31)	7.4 (m, 3H, Ar-H), 7.65 (m, 2H, Ar-H), 7.75 (d, 1H, *J* = 4.2), 7.9 (d, 2H, *J* = 8.4), 7.95 (d, 1H, *J* = 4.2), 8.25 (d, 2H, *J* = 8.4)
Ib, j	$C_{17}H_{13}NO_2Se$	42	110 (MeOH)	59.64 (59.81	3.80 3.92	4.09 4.18)	2.35 (s, 3H, $C\underline{H}_3$), 7.25 (d, 2H, *J* = 7), 7.6 (d, 2H, *J* = 7), 7.75 (d, 1H, *J* = 4.2), 7.9 (d, 2H, *J* = 8.4), 8.0 (d, 2H, *J* = 4.2), 8.3 (d, 2H, *J* = 8.4)
Ic, j	$C_{17}H_{13}NO_3Se$	41	178 (MeCN)	56.98 (57.26	3.63 3.78	3.91 3.99)	3.8 (s, 3H, $OC\underline{H}_3$), 7.0 (d, 2H, *J* = 7.7), 7.5 (d, 2H, *J* = 7.7), 7.65 (d, 1H, *J* = 4.2), 7.85 (d, 2H, *J* = 8.4), 7.95 (d, 1H, *J* = 4.2), 8.3 (d, 2H, *J* = 8.4)
Id, j	$C_{16}H_{10}FNO_2Se$	37	151 (MeCN)	55.49 (55.72	2.89 2.96	4.05 4.01)	7.35 (m, 2H, Ar-H), 7.6 (m, 2H, Ar-H), 7.7 (d, 1H, *J* = 3.5), 7.85 (d, 2H, *J* = 8.4), 7.95 (d, 1H, *J* = 3.5)
Ie, j	$C_{16}H_{10}ClNO_2Se$	43	143 (MeOH)	52.96 (53.24	2.75 2.88	3.86 4.02)	7.45 (d, 2H, *J* = 7.7), 7.7 (d, 2H, *J* = 7.7), 7.8 (d, 1H, *J* = 3.5), 7.85 (d, 2H, *J* = 8.4), 7.95 (d, 1H, *J* = 3.5), 8.3 (d, 2H, *J* = 8.4)
If, j	$C_{16}H_{10}BrNO_2Se$	42	194 (MeCN)	47.17 (47.08	2.45 2.53	3.43 3.49)	7.65 (s, 4H, Ar-H), 7.8 (d, 1H, *J* = 4.2), 7.9 (d, 2H, *J* = 8.4), 8.0 (d, 1H, *J* = 4.2), 8.3 (d, 2H, *J* = 8.4)

TABLE III

U.V. spectroscopy

Compound	Ia, g	Id, g	Ie, g	Ia, h	Ib, h	Ic, h	Id, h	Ie, h	If, h	Ia, i	Ib, i	Ic, i	Id, i	Ie, i	If, i	Ia, j	Ib, j	Ic, j	Id, j	Ie, j	If, j
λ max (nm)	348	348	332	348	352	360	348	332	328	355	352	364	360	379	358	368	388	400	379	380	381
ε	6900	5100	19000	9500	49000	5100	5500	30400	39000	16000	5200	9000	10500	15500	17500	5500	49000	5100	9600	19100	40600

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