PAPERS

Pyrrole Studies; 34[1]. Synthesis of 1,2-Di(2-pyrrolyl)ethenes and Related Compounds

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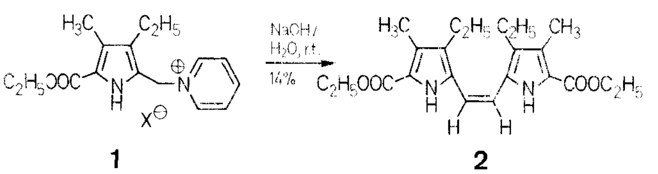
Novel 1,2-Di(2-pyrrolyl)ethenes **5** and related compounds **8** have been prepared in good yield using the Wittig reaction. Although the Horner reaction can be used for the synthesis of 1,2-di(2-thienyl)- and 1,2-di(2-furyl)-ethenes, the procedure is not suitable as a viable route for the preparation of the corresponding dipyrrolylethenes.

In the course of our synthetic studies of 10*a*,21-didehydro-10*a*-homocorrole[2] and of other polypyrroles[3-6] we required 1,2-di(2-pyrrolyl)ethenes **5a, b**. Only one derivative of such a system has been reported previously[7], when the (*E*)-isomer of the polysubstituted compound (**2**) was isolated in low yield *via* the base-catalysed reaction of the 1-(2-pyrrolylmethyl)pyridinium salt (**1**). However, our experience with the synthesis of 2-vinyl-[8] and 2-styryl-[8,9] pyrroles led us to believe that higher yields might result from the Wittig reaction e.g. **3b** + **4b** → **5b** in a manner analogous to that described for the synthesis of the corresponding difuryl- and dithienyl-ethenes[10]. The formylpyrroles are easily obtained through the Vilsmeier-Haack reaction[11] and the 2-(pyrrolylmethyl)phosphonium salts are readily available *via* the nucleophilic displacement reaction with triphenylphosphine on the trimethylammonium salts[12], which can be obtained *via* the Mannich reaction on the corresponding 2-unsubsituted pyrroles. The analogous reactions of the (pyrrolylmethyl)phosphonium salts with furan- and thiophene-2-aldehydes produced the corresponding 1-(2-furyl)-2-(2-pyrrolyl)- and 1-(2-pyrrolyl)-2-(2-thienyl)-ethenes (Table 1).



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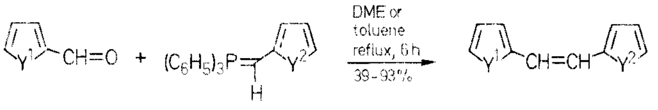
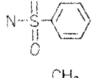
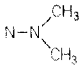
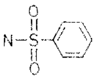
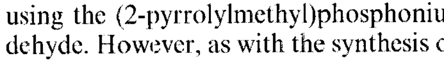


3 **4** **5a-l**

5	Y^1	Y^2	5	Y^1	Y^2
a	NH	N–CH$_3$	**g**	S	N–CH$_2$–OCH$_3$
b	N–CH$_3$	N–CH$_3$	**h**	NH •	O
c		N–CH$_3$	**i**	NH	S
d		N–CH$_3$	**j**	N–CH$_3$	O
e	NH	N–CH$_2$–OCH$_3$	**k**	N–CH$_3$	S
f	O	N–CH$_2$–OCH$_3$	**l**		S

As noted during the synthesis of the styrylpyrroles[9], better yields of the heteroarylethenes were obtained when the phosphoranes were generated using sodium hydride in preference to sodium ethoxide. A limiting feature of the procedure, however, was the observation that, for optimum yields, it was necessary to protect the nitrogen atom of the (2-pyrrolylmethylene)phosphoranes. A simple rationalisation of this requirement is that, as there is no stabilisation of the carbanionic centre by the pyrrolyl ring, an equilibrium between the pyrrolyl anion and the ylide **6** ⇌ **7** reduces the effective reactivity of the ylide. In contrast, it is noteworthy that, in spite of the greater acidity of the NH group of 2-formylpyrrole compared with the (2-pyrrolylmethyl) phosphonium salts, 2-formylpyrrole undergoes the Wittig reaction, albeit in relativity lower yields than the corresponding reactions of the 1-substituted 2-formylpyrroles with benzylydene[8,9], (1-methyl-2-pyrrolylmethylene)-, 2-thienylmethylene-, and 2-furylmethylene-phosphoranes. These observations indicate that the NH acidity of the (2-pyrrolylmethylene) phosphorane is greater than the NH acididites of both the (2-pyrrolylmethyl)phosphonium salt and 2-formylpyrrole.



6 **7**

The 1-substituted 2-styrylpyrroles **8a–e** were prepared in good yield from benzyltriphenylphosphonium bromide and the appropriate heteroaryl aldehyde **3a–e** using procedures analogous to those described earlier[8,9] and, in all cases, the (*E*)-isomers predominated. It was also found that the (*E*)-2-styrylpyrroles could be obtained by the alternative procedure using the (2-pyrrolylmethyl)phosphonium salt and benzaldehyde. However, as with the synthesis of the dipyrrolylethenes, good yields were obtained only for the protected 1-substituted pyrrolyl derivatives (Table 2). The (*E*)-/(*Z*)-isomer ratios, quoted in Tables 1 and 2, were determined on the crude reaction products, using ^{1}H-N.M.R. spectroscopy. Where the isomer ratio was greather than *ca.* 15:1, the ^{1}H-N.M.R. data were unreliable and, generally, only the (*E*)-isomers were obtained from the reaction mixtures. Application of the Horner reaction to the synthesis of 1,2-(heteroaryl)ethenes showed the procedure to be superior to the previously reported Wittig reaction for the preparation of the dithienyl- and difuryl derivatives[10]. However, in contrast, the procedure was not suitable for the synthesis of the dipyrrolylethenes. Diethyl 2-pyrrolylmethylphosphonate **10a** was obtained in low yield (10%) from the reaction of trimethyl(2-pyrrolylmethyl)ammonium iodide **9a** with

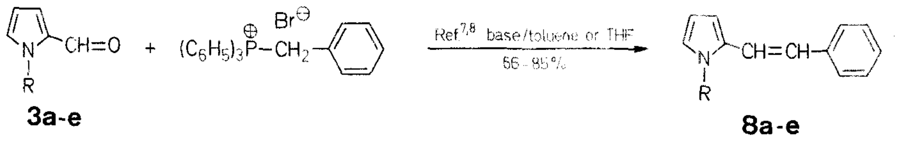


Table 1. Wittig Synthesis of 1,2-Di(2-pyrrolyl)ethenes and Related Compounds **5**

Product No.	Method	Yield[a] [%]	Ratio[b] of (*E*)–/(*Z*)–	Molecular Formula[c]	(Isomer) m.p. [°C] or b.p. [°C]/torr	U.V. (EtOH) λ_{max} (log ε)	^{1}H-N.M.R. (CDCl$_3$/TMS) δ [ppm] —CH=CH—		*J*(Hz)q
5a	A	39	1.2 : 1	$C_{11}H_{12}N_2$ (172.2)	(*E*)–m.p. 118–120°	219 (3.83), 338 (4.39)	6.70	6.48	16.3
					(*Z*)–oil	200 (4.08), 318 (4.09)	6.39	5.97	12.0
5b	B	76	14 : 1	$C_{12}H_{14}N_2$ (186.2)	(*E*)–m.p. 149–150°	231 (3.76), 344 (4.23)	6.75	6.75	–
					(*Z*)–oil	214 (4.08), 328 (4.19)	6.26	6.26	–
5c	A	80	–[d]	$C_{17}H_{16}N_2O_2S$ (312.4)	(*E*)–m.p. 138–141°	220 (4.07), 354 (3.80)	7.08	6.83	15.7
5d	B	51	–[d]	$C_{13}H_{17}N_3$ (215.3)	(*E*)–b.p. 115°/0.1	225 (3.97), 340.5 (4.14)	7.02	6.79	16.3
5e	A	81	6.1 : 1	$C_{12}H_{14}N_2O$ (202.2)	(*E*)–m.p. 78°	205 (2.81), 338 (4.40)	6.68	6.68	–
					(*Z*)–b.p. 100°/0.1	207 (4.22), 321 (4.30)	6.42	6.08	12.35
5f	A	64	–[d]	$C_{12}H_{13}NO_2$ (203.2)	(*E*)–b.p. 100°/0.1	221 (3.81), 335 (4.39)	7.00	6.65	16.0
5g	A	62	–[d]	$C_{12}H_{13}NOS$ (219.3)	(*E*)–b.p. 100°/0.1	245 (3.88), 345 (4.40)	7.02	6.82	16.9
5h	A	62	2.7 : 1	$C_{10}H_9NO$ (159.2)	(*E*)–m.p. 104°	203 (3.89), 330 (4.52), 342 (4.45)	6.87	6.43	16.0
					(*Z*)–m.p. 72–73°	226 (4.14), 329 (4.39), 345 (4.32)	6.21	5.88	13.6
5i	A	50	2.3 : 1	$C_{10}H_9NS$ (175.2)	(*E*)–m.p. 141–144°	248 (3.68), 344 (4.38)	6.76	6.76	–
					(*Z*)–m.p. 57–60°	248 (3.86), 342 (4.08)	6.38	6.23	12.5
5j	B C	86 90	–[d]	$C_{11}H_{11}NO$ (173.2)	(*E*)–m.p. 34–36° b.p. 92–94°/0.15	332 (3.92), 350 inf. (3.74)	6.90	6.61	15.95
5k	B C	45 93	–[d]	$C_{11}H_{11}NS$ (189.3)	(*E*)–m.p. 65–66° b.p. 106–112°/1.0	250 (3.81), 336 (3.87)	6.98	6.72	15.9
5l	A	53	–[d]	$C_{16}H_{13}NO_2S_2$ (315.4)	(*E*)–m.p. 61–62.5°	230 (4.15), 321 (3.97)	7.05	6.78	16.0

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[a] Overall yield.

[b] Isomer rations were estimated by ^{1}H-N.M.R. spectroscopy on the crude reaction products. Where the (*E*)/(*Z*)-isomer ratio was greater than *ca.* 15 : 1 the ^{1}H-N.M.R. data were unreliable and only the (*E*)-isomers were isolated.

[c] The microanalyses were in good agreement with the calculated values: C ± 0.4, H ± 0.4, N ± 0.2.

[d] Only the (*E*)-isomer was isolated.

Table 2. Wittig Synthesis of 1-Substituted 2-styrylpyrroles **8**

Product No.	R	Method	Yield[a] [%]	Ratio of (*E*)-/(*Z*)-[b]	(Isomer)-m.p. [°C] or b.p. [°C]/torr	Molecular Formula[c] or Lit. Data	U.V. (EtOH) λ_{max} (logε)	^{1}H-N.M.R. (CDCl$_3$/TMS) δ [ppm] —CH=CH—		*J* (Hz)
8a	H	A	45	2.75 : 1	(*E*)-m.p. 141–142°	m.p. 140–142°[8]	237 (3.75), 330 (4.38),	6.97	6.6.60	16.9
		B	68	~ 1 : 1	(*Z*)-b.p. 140°/1	b.p. 141–144°/1.5[8]	228 (4.05), 315 (3.95)	6.35	6.35	–
		C	77	~ 1 : 1						
		D	23	–[d]						
8b	CH_3	A	85	~ 3 : 1	(*E*)-m.p. 71–72°	m.p. 71–73°[8]	237 (3.95), 338 (4.27),	6.90	6.88	–
					(*Z*)-b.p. 136°/1.0	b.p. 136–139°/2.0[8]	233 (4.14), 322 (4.01)	–	–	–
8c	$N(CH_3)_2$	A	66	–[d]	(*E*)-m.p. 102–103°	$C_{14}H_{16}N_2$ (212.3)	235 (4.03), 331 (4.27)	7.08	6.84	15.5
8d	$SO_2C_6H_5$	A	65	–[d]	(*E*)-m.p. 75–77°	$C_{18}H_{15}NO_2S$ (309.4)	225 (4.16), 318 (4.11)	–[e]	6.78	15.0
8e	CH_2OCH_3	D	73	–[d]	(*E*)-m.p. 36–37°	$C_{14}H_{15}NO$ (213.3)	237 (3.94), 335 (4.05)	7.09	6.87	16.5

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[a] Overall yield.

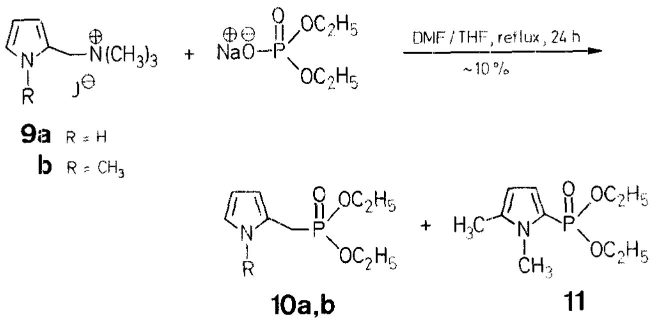
[b] Isomer ratios were estimated by ^{1}H-N.M.R. spectroscopy on crude reaction products.

[c] Satisfactory microanalyses obtained: C ± 0.2, H ± 0.2, N ± 0.1.

[d] Only the (*E*)-isomer was isolated.

[e] Obscured by phenyl signals.

sodium diethyl phosphite, whilst an analogous reaction of the 1-methyl derivative gave a ca. 2:1 mixture of the isomers **10b** and **11**, which could not be readily separated, in an overall yield of only 15%.



Finally, 1,2-di(2-furyl)- and 1,2-di(2-thienyl)-ethenes could be successfully prepared by the Horner reaction of the corresponding diethyl (heteroarylmethyl)phosphonates with heteroaryl aldehydes using sodium hydride as the base (see experimental).

1-Dimethylaminopyrrole[13], 2-formylpyrrole (**3a**)[14], 2-formyl-1-methylpyrrole (**3b**)[14], benzyltriphenylphosphonium bromide[15], (2-pyrrolylmethyl)triphenylphosphonium bromide[12] and (1-methyl-2-pyrrolyl)triphenylphosphonium bromide[12] were prepared according to the procedure described in the literature.

1-Benzenesulphonyl-2-formylpyrrole (3c):

2-Formylpyrrole (**3a**; 1.8 g, 20 mmol), benzenesulphonyl chloride (5.3 g, 30 mmol) and tetra-*n*-butylammonium bromide (0.2 g) in dichloromethane (10 ml) are stirred with 30% aqueous sodium hydroxide (5 ml, 37 mmol) at 15 °C for 24 h. The organic phase is separated and the aqueous phase is extracted with dichloromethane (2 × 20 ml). The combined organic layer is washed with water (3 × 20 ml), dried with magnesium sulfate and evaporated. Chromatographic purification of the residual solid from Kieselgel using chloromethane as the eluent gives **3c**; yield: 4.5 g (96%); m.p. 79.5–80.5 °C.

$C_{11}H_9NO_3S$	calc.	C 56.2	H 3.85	N 5.95	S 13.6
(235.3)	found	56.2	3.70	5.95	13.7

1-Dimethylamino-2-formylpyrrole (3d): Phosphorus oxychloride (6.1 g, 40 mmol) is added to 1-dimethylaminopyrrole (4.4 g, 40 mmol) and dimethylformamide (30 g, 41 mmol) in hexane/diethyl ether (5:2, 14 ml) at 0 °C. After the reaction mixture has been stirred at 0 °C for 1 h and at 15 °C for an additional 1 h, it is poured onto ice (50 g) and sodium hydroxide (8 g), and then allowed to stand for 1 h. The mixture is extracted with diethyl ether (3 × 60 ml), the combined extract is dried with magnesium sulfate and evaporated to give **3d**; yield: 3.1 g (56%); b.p. 84–86 °C/15 torr.

$C_7H_{10}N_2O$	calc.	C 60.85	H 7.3	N 20.3
(138.2)	found	60.7	7.5	20.3

(1-Methoxymethyl-2-pyrrolylmethyl)triphenylphosphonium Bromide:

1-Methoxymethylpyrrole: Pyrrole (38.0 g, 570 mmol) in dimethylformamide (50 ml) is added to sodium hydride (14.4 g, 600 mmol) in dimethylformamide (250 ml) at 0 °C and the mixture is stirred for 2 h. Chloromethyl methyl ether (56 g, 800 mmol) in dimethylformamide (50 ml) is then added at 0 °C. The reaction mixture is kept at 15 °C for 6 h and then poured onto ice (500 g). The aqueous layer is extracted with diethyl ether (3 × 50 ml) and the combined organic phase is dried with magnesium sulfate and evaporated to give 1-methoxymethylpyrrole; yield: 38.7 g (62%); b.p. 76–78 °/47 torr.

C_6H_9NO	calc.	C 64.8	H 8.2	N 12.6
(111.2)	found	64.9	8.3	12.7

1-Methoxymethyl-2-dimethylaminopyrrole: Dimethylammonium chloride (13.5 g, 170 mmol) and aqueous formaldehyde (40%, 15 g, 195 mmol) are added dropwise to 1-methoxymethylpyrrole (9.3 g, 84 mmol) at 0 °C and the mixture is stirred at 0 °C for 6 h and then at 15 °C for 15 h. The mixture is cooled to 0 °C, made strongly basic by the addition of aqueous sodium hydroxide (10%), and extracted with diethyl ether (2 × 25 ml). The combined ether extract is dried with magnesium sulfate and evaporated to give 1-methoxymethyl-2-dimethylaminopyrrole; yield: 7.4 g (52%); b.p. 80.5 °C/15 torr.

$C_9H_{16}N_2O$	calc.	C 64.2	H 9.6	N 16.65
(168.2)	found	63.9	9.7	16.7

Conversion of 1-Methoxymethyl-2-dimethylaminopyrrole to (1-Methoxymethyl-2-pyrrolmethyl)triphenylphosphonium Bromide: Bromoethane (7.0 g, 70 mmol) is added to the dimethylaminomethylpyrrole (9.5 g, 57 mmol) in diethyl ether (100 ml) and the mixture is kept in a sealed flask at 4 °C for 3 days. The solvent and excess bromoethane are removed under reduced pressure and triphenylphosphine (15 g, 57 mmol) in methanol (150 ml) is added to the ammonium salt. After the mixture has been heated under reflux for 16 h, it is concentrated and the precipitated solid is collected. Recrystallisation from 1,2-dichloroethane gives (1-methoxymethyl-2-pyrrolylmethyl)triphenylphosphonium bromide; yield: 15.4 g (58%); m.p. 208–210 °C.

$C_{25}H_{25}BrNOP \cdot C_2H_4Cl_2$	calc.	C 61.2	H 5.5	N 2.6
(565.3)	found	61.6	5.4	2.6

Wittig Synthesis of 1,2-di(2-pyrrolyl)ethenes and Related Compounds 5; General Procedure:

Method A: The appropriate heteroarylmethylphosphonium salt (22 mmol) is added to a stirred suspension of sodium hydride (0.53 g, 22 mmol) in toluene (150 ml) and the mixture is stirred for 30 min before the addition of the heteroaryl aldehyde (**3**; 20 mmol). The mixture is heated at 80 °C for 6 h and then cooled to room temperature and filtered. The organic phase is dried with magnesium sulfate and evaporated. The crude diheteroarylethene is purified by chromatography from Merck Kieselgel 60 using dichloromethane petroleum ether (2:1) as the eluent.

Method B: The procedure used is analogous to that described in Method A, except that the reaction is conducted under reflux in dimethoxyethane (100 ml) in place of toluene as the solvent.

Wittig Synthesis of 2-styrylpyrroles 8; General Procedure:

Method A: Benzyltriphenylphosphonium bromide (4.27 g, 11 mmol) is added to a stirred suspension of sodium hydride (0.26 g, 11 mmol in toluene (50 ml) and the mixture is stirred at 15 °C for 30 min. The appropriate 1-substituted 2-formylpyrrole (**3a–e**; 10 mmol) is added and the mixture is heated under reflux for 3 h. The solvent is removed under reduced pressure and the styrylpyrrole is purified by chromatography from Merck Kieselgel 60 using dichloromethane petroleum ether (2:1) as the eluent.

Method B: The formylpyrrole (**3a–e**; 20 mmol) in toluene (20 ml) is added dropwise to a stirred suspension of benzyltriphenylphosphonium bromide (8.6 g, 22 mmol) and sodium ethoxide (from 0.58 g of sodium) in toluene (60 ml). The solvent is removed under reduced pressure and the crude reaction product is purified as described in Method A.

Method C: The procedure used is analogous to that described in Method B, except that the reaction is conducted in tetrahydrofuran (60 ml) in place of toluene as the solvent.

Method D: The appropriate (2-pyrrolymethyl)triphenylphosphonium bromide (**4e**; 11 mmol) is added with stirring to sodium hydride (0.26 g, 11 mmol) in tetrahydrofuran (50 ml) and the mixture is stirred at 15 °C for 30 min. Benzaldehyde (1.06 g, 10 mmol) is added and the mixture is heated under reflux for 3 h. The styrylpyrrole is isolated and purified as described in Method A.

Diethyl (2-Furylmethyl)phosphonate:

Furfuryl chloride (5.0 g, 43 mmol) and triethyl phosphite (8.3 g, 50 mmol) are heated under reflux for 5 h and then kept at 15 °C for 12 h. Distillation gives diethyl (2-furylmethyl)phosphonate; yield: 6.5 g (62%); b.p. 90 °C/0.1 torr.

$C_9H_{15}O_4P$	calc.	C 49.5	H 7.0
(218.2)	found	49.4	7.1

Diethyl (2-Thienylmethyl)phosphonate:
2-Chloromethylthiophene (8.3 g, 63 mmol) and triethyl phosphite (12.0 g, 72 mmol) are heated under reflux for 10 h and then kept at 15 °C for 12 h. Distillation gives diethyl (2-thienylmethyl)phosphonate; yield: 7.4 g (46%); b.p. 112 °C/0.15 torr.

$C_9H_{15}O_3PS$	calc.	C 46.2	H 6.5	S 13.7
(234.3)	found	46.2	6.5	13.9

Diethyl (2-Pyrrolylmethyl)phosphonate (10a): 2-Dimethylaminomethylpyrrole (20.0 g, 16 mmol) and iodomethane (25.6 g, 18 mmol) in diethyl ether (150 ml) are kept at 0 °C for 72 h. The solvent and excess iodomethane are removed under reduced pressure and the crude trimethylammonium salt (42.8 g) is added, without further purification, to sodium diethylphosphite (32.2 g, 200 mmol) in dimethylformamide (200 ml) and tetrahydrofuran (200 ml). The reaction mixture is heated under reflux for 24 h and then concentrated to one-third volume. Water (150 ml) is added and the mixture is extracted with diethyl ether (3 × 50 ml). The combined ether extract is dried with magnesium sulfate and evaporated. Distillation and chromatographic purification of the product from Kieselgel, using ethyl acetate as the eluent, gives **10a**; yield: 3.4 g (9.8%); b.p. 102–104 °C/0.01 torr.

$C_9H_{16}NO_3P$	calc.	C 49.80	H 7.40	N 6.45
(217.2)		49.6	7.55	6.30

^{1}H-N.M.R. (CDCl$_3$/TMS): $\delta = 1.15$ (t, 3 H, $CH_2C\underline{H}_3$, $J = 6.9$ Hz); 3.19 (d. 2 H, CH_2—P, $J = 20.2$ Hz); 3.99 (overlapping q, 2 H, $C\underline{H}_2$—CH_3), 6.05 (m, 2 H); 6.64 ppm (m, 1 H).

Attempted synthesis of diethyl (1-methyl-2-pyrrolylmethyl)phosphonate (**10b**): 1-Methyl-2-dimethylaminopyrrole (**9b**; 20.0 g, 14 mmol) and iodomethane (23.0 g, 16 mmol) in diethyl ether (100 ml) are kept at 0 °C for 72 h. The solvent and excess iodomethane are removed under reduced pressure and the crude trimethylammonium salt (40.0 g) is added, without further purification, to sodium diethyl phosphite (29.0 g, 180 mmol) in dimethylformamide (200 ml) and tetrahydrofuran (200 ml). The reaction mixture is heated under reflux for 24 h and the product isolated using the procedure described above. An isomeric mixture of **10b** (*a*) and **11**(*b*) obtained in a ratio of 2:1 as indicated by ^{1}H-N.M.R. data; yield: 4.9 g (15%); b.p. 160 °C/15 torr.

$C_{10}H_{18}NO_3P$	calc.	C 51.90	H 7.85	N 6.10
(231.2)	found	51.90	8.05	6.00

^{1}H-N.M.R. (CDCl$_3$/TMS): $\delta = 1.21$ (t, $CH_2C\underline{H}_3$, *a*); 1.28 (t, $CH_2C\underline{H}_3$, *b*); 2.18 (s, C—CH_3, *b*); 3.11 (d, CH_2—P, $J = 20.1$ Hz, *a*); 3.56 (s, N—CH_3, *a*); 3.63 (s, N—CH_3, *b*); 4.0 (overlapping q, CH_2—CH_3, *a*, *b*); 5.89 (m, *b*); 5.57 (d, *a*); 6.27 (d, *b*); 6.66 ppm (t. *a*).

Horner Synthesis of 1,2-Di(heteroaryl)ethenes; General Procedure: Sodium hydride (0.24 g) is added with stirring to the appropriate diethyl (heteroarylmethyl) phosphonate (10 mmol) in dimethoxyethane (50 ml) at 15 °C and the appropriate heteroaryl aldehyde (10 mmol) is added dropwise. The mixture is heated under reflux for 3 h and then poured into water (50 ml). The aqueous mixture is extracted with diethyl ether (3 × 20 ml), the combined ether layer is dried with magnesium sulfate and evaporated to give the ethene.

(*E*)-1,2-di(2-furyl)ethene; yield: 65%; m.p. 97–99 °C (Lit.[9], m.p. 99.5–100 °C).

(*E*)-1,2-di(2-thienyl)ethene; yield: 94%; m.p. 131–132 °C (Lit.[9], m.p. 132–133.5 °C).

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