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POLYENYL-SUBSTITUTED FURANS AND THIOPHENES. A STUDY OF THE ELECTRONIC SPECTRA—I[1]

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Abstract—The synthesis and electronic spectra of a series of polyenyl-substituted furans and thiophenes are described. With respect to the first electronic transition of these and related furan and thiophene derivatives the net contribution of the heterocyclic ring is roughly equal to that of a butadiene unit. This is in contrast with known spectral data of compounds where the thiophene ring is part of a larger condensed ring system.

Introduction

THE UV spectra of furan and thiophene and derivatives have already been the subject of many investigations, which can roughly be divided into three groups:

(i) Empirical studies of the spectra of substituted furans and thiophenes, without quantummechanical calculations. These concern mostly compilations of spectral data of compounds with polar functional groups.[2–6]

(ii) Theoretical papers on furan and thiophene, with attempted correlation between calculated and experimental spectra. Both HMO[7, 8] and SCF-MO[9–15] methods have been used.

(iii) Studies as under (ii) on derivatives of furan and thiophene in which the heterocyclic ring is part of a larger condensed ring system.[16–18]

For a theoretical study of the UV spectra of non-condensed derivatives of furan and thiophene we thought it useful to investigate polyenyl-substituted compounds. This class of substances seemed well suited for this aim, because the hererocyclic system is extended with C=C double bonds only, so that in the theoretical approach the parametrisation problem is minimal. Furthermore, the theoretical studies can be compared with experimental data of a large group of structurally related compounds. This is an important point in any correlation between experimental and calculated data.

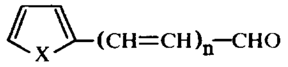
The compounds studied have the general formula **1** and **2** with either n or both n and m varying from 1 to 3. Of both series only the members **a** and **b** have been reported before. This paper describes the synthesis and the electronic spectra of the series **1a–f** and **2a–f**; the theoretical aspects are dealt with in Part II.

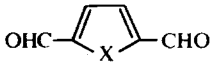
1: X = O
2: X = S

a: m = 0, n = 1 **d**: m = n = 1
b: m = 0, n = 2 **e**: m = n = 2
c: m = 0, n = 3 **f**: m = n = 3

Synthesis

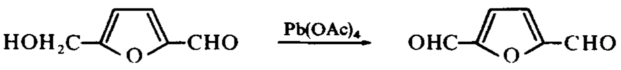
With the exception of **1a**—which was made by decarboxylation of furylacrylic acid[19]—the title compounds were obtained by Wittig reactions between aldehydes **3**–**6** and appropriate alkyltriphenylphosphonium bromides.





3: n = 0 **a**: X = O **6a**: X = O
4: n = 1 **b**: X = S **b**: X = S
5: n = 2

The aldehydes were prepared by known methods, except furan-2,5-dicarboxaldehyde (**6a**). For the preparation of **6a** from 2,5-bis(chloromethyl)furan, described by Yur'ev *et al.*,[20] we found an attractive alternative in the oxidation of 5-(hydroxymethyl)furfural (**7**) with lead tetraacetate in pyridine.[21],*



7 **6a**

The starting material for this reaction (**7**) is easily obtained from sucrose.[22, 23]

The phosphonium bromides used in the Wittig reaction were methyl-, allyl-, and 2,4-pentadienylphosphonium bromide (**8**, **9** and **10**). The latter compound, hitherto unknown, was prepared from triphenylphosphine and 1-bromo-2,4-pentadiene.[24]

$Ph_3\overset{+}{P}\text{-}CH_2\text{-}(CH{=}CH)_nH\ Br^-$

8: n = O
9: n = 1
10: n = 2

Of the many known procedures[25–29] for carrying out the Wittig reaction, several were tried. In the course of our investigations we found that the choice of ether as solvent for the monofunctional compounds, and 1,2-dimethoxyethane for the bifunctional compounds, gave the best results, in combination with sodium methoxide as the basic reagent.[30] The crude products were freed from polar contaminants by rapid chromatography of a pentane solution over silica gel or neutral alumina. During this process some polymerization occurred on the column.

The compounds **1a-e** and **2a-e** were obtained as analytically pure substances by distillation. They are very reactive, and polymerize readily when exposed to atmospheric oxygen. The reactivity is exemplified by 2,5-di-(1,3-butadienyl)furan (**1e**), which reacted explosively with pure oxygen in a combustion analysis experiment. However, when stored under nitrogen, the compounds can be kept for some time.

The highest members of each series, **1f** and **2f**, were not isolated, but identified by their UV spectra, which were measured in the dilute pentane solution, obtained after chromatography.

Stereochemistry

The Wittig reaction in general gives rise to a mixture of *cis* and *trans* isomers around

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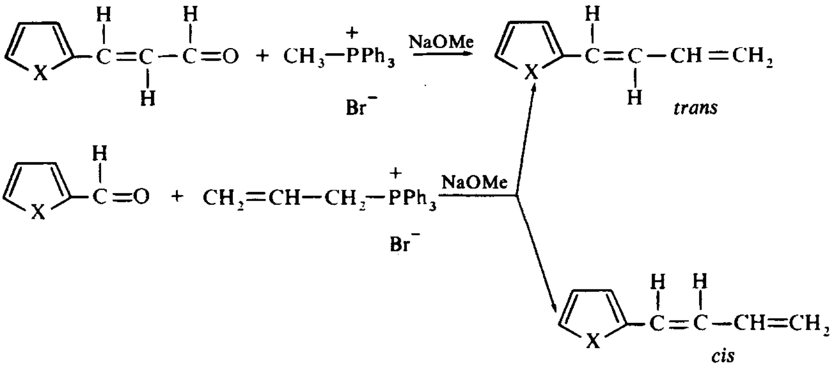
* We found that in this oxidation the amount of pyridine can be reduced to one fifth of the rather large quantity recommended by Partch, if the reaction mixture is cooled in ice.

the double bond formed during the reaction.[29] This was found to occur also in the preparation of the title compounds, except, of course, those reactions in which methyltriphenylphosphonium bromide was used.

The stereochemistry of the products was of interest to us, because of its possible influence on the electronic spectra. For two compounds, **1b** and **2b**, representing the simplest case of geometrical isomerism in this series, the two isomers could be identified. This could be done because one of the two possible Wittig reactions leading to **1b** or **2b** starts with the aldehyde **4**, in which the *trans* double bond is already present.[31, 32] The aldehyde **3** gives an isomer mixture.



For **1b** and **2b** evaluation of the *cis-trans* product ratio of the second reaction was possible by glc over a capillary column, using the pure *trans* product of the first reaction to identify the peaks.

For 2-(1,3,5-hexatrienyl)furan (**1c**) and its thiophene analogue **2c** the same method was followed. The all-*trans* compounds were synthesized from the aldehydes **5**.*[31, 32] Preparation from the other aldehydes **3** and **4** gave isomer mixtures. This could be seen from the NMR spectra of the products, which were all more complex than those of the all-*trans* compounds. The exact composition of these mixtures, however, could not be fixed unequivocally as the isomers could not be separated by GLC.

The influence of the presence of *cis* isomers on the spectra is discussed below.

Electronic spectra

It would be of interest to see whether the extension of the π-electron system of the heterocyclic ring with polyenic side chains, as in the title compounds, would impart a more or less polyenic character to the whole system. Therefore a comparison between the electronic spectra of the series **1** and **2** and those of linear conjugated polyenes[33] **11** seems appropriate.

$$H(CH{=}CH)_nH$$

11

The title compounds show a characteristic long wavelength band, with fine structure. The spacing of the vibrational levels is 1450 (± 150) cm^{-1} for the furan compounds **1**, which is the same as that reported[33] for linear polyenes **11**. For the thiophene compounds **2** only a few reliable measurements are possible, giving a spacing of 1250 (± 150) cm^{-1}.

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* The double bond in condensation products like **4** and **5** generally has the *trans* configuration.[31, 32]

The maxima at longest wavelength are given in Table I for the series **1**, **2** and **11**. Because of the vibrational fine structure the values in Table I refer to the longest wavelength peak or shoulder, those being closest to the 0–0 transition.* For members of the series where the fine structure is not well resolved, the value is approximate. (For the compounds **1c**, **e**, **f** and **2c**, **e**, **f** additional bands at shorter wavelengths are found. The full spectra of all title compounds are given in numerical form in the Experimental, and in graphical form in Fig. 1 and 2 of the following paper (Part II)).

Table 1. Position of the longest wavelength absorption maximum (mμ)

Polyenylfurans[a] (**1**)		Polyenylthiophenes[a] (**2**)		Polyenes[b] (**11**)	
1a	272·5	**2a**	275[c]	n = 3	268
1b	306	**2b**	315[d]	4	304
1c	336	**2c**	346	5	334
1d	318	**2d**	328[d]	4	304
1e	371·5	**2e**	381	6	364
1f	419	**2f**	422	8	410

[a] For more detailed information concerning these spectra see Figs. 1 and 2 of Part II and Experimental Section. Solvents were isooctane (for **1**) and cyclohexane (for **2**).

[b] Data taken from ref. 33; solvent isooctane.

[c] This spectrum shows no fine structure.

[d] Approximate value.

Two conclusions can be drawn from Table 1. First, the absorption wavelengths, which differ appreciably for unsubstituted furan (λ_{max} 205 mμ[34]) and thiophene (λ_{max} 231 mμ[34]) are much closer together for the polyenyl-substituted furans and thiophenes of series **1** and **2**. As the conjugated system becomes longer, this difference (in mμ) remains approximately constant, or decreases. This means that, on an energy scale, the data for the series **1** and **2** converge. Apparently, in the compounds with longer side chains the difference in electronic behaviour between the furan ring and the thiophene ring tends to be overshadowed by the common polyenic part of the molecule.

Second, when the data are compared for compounds, in which the same *total* number of double bonds is present (i.e. including the two ring double bonds in **1** and **2**), a rough agreement is found between the data of the polyenylfurans and -thiophenes on one hand and the data of the linear polyenes **11** on the other hand.

For furan derivatives this is a regularity which has been noted earlier by Hausser and Kuhn,[4] who compared furylpolyene aldehydes and acids with linear polyene aldehydes and acids. A similar observation was also made by Wynberg and Van Reijendam[35] in connection with the spectra of bifurans. They found that the large difference in absorption wavelength between 2,2′-bifuran (295 mμ) and 3,3′-bifuran (231 mμ) has a parallel in the behavior of the corresponding polyenic substances, 1,3,5,7-octatetraene (λ_{max} 304 mμ) and 2,3-divinyl-1,3-butadiene (λ_{max} 223 mμ).

For thiophene derivatives this type of regularity has not been noted before. However, a collection of literature data concerning spectra of thiophenes with extended conjugation in the 2-position reveals that also for a wider group of compounds than

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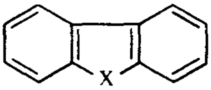
* A comparison based on the wavelength of the main maxima leads to similar conclusions.

series **2** the wavelengths of maximum absorption can very well be compared with those of corresponding polyenic substances (see Appendix).

The general agreement in position and shape of the long wavelength absorption band for the series **1**, **2** and **11** seem to indicate that, with respect to the first electronic transition, the heteroatom in **1** and **2** is of relatively little importance, and the hererocyclic ring behaves like a butadiene unit.

It is interesting to note that a different situation exists in compounds where a five-membered heterocyclic ring is part of a larger condensed ring system, as in **12** and **13**. The nature of the heteroatom has a much greater influence on the spectrum here than in the series **1** and **2**.[36, 37] e.g. The long wavelength absorption band at 305–330 mμ in the spectrum of dibenzothiophene (**12**, X = S) is shifted to below 300 mμ in the case of the oxygen analogue dibenzofuran, whereas for carbazole (**12**, X = NH) it occurs at 320–340 mμ. Similar effects are also visible in the long wavelength part of the spectra of **13** and related substances.[36, 37]



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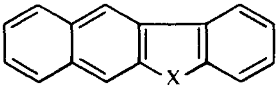

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This indicates that the role of the heteroatom is a very different one in series **1** and **2** on one hand, and substances like **12** and **13** on the other hand. The theoretical background of this behaviour is discussed in Part II.

The influence of *cis-trans* isomerism on the spectra can be seen quantitatively in the cases of 2-(1,3-butadienyl)furan (**1b**) and its thiophene analogue **2b**. As the data for the *trans* compounds are known, the spectra of the isomer mixtures with known composition allow calculation of the spectra of the *cis* isomers. These data are given in Table 2.

TABLE 2. UV SPECTRA[a] OF *cis*- AND *trans*-**1b** AND **2b**

	maxima	minima
trans-**1b**	306 (28·3), 292 (35·7)	302 (26·4), 232 (2·51)
cis-**1b**[b]	306 (19·8), 292 (25·4)	303 (18·7), 232 (1·56)
trans-**2b**	304 (22·7), 216 (14·0)	236 (2·60)
cis-**2b**[b]	306 (15·0), 217 (12·3)	242 (1·52)

[a] Presented as λ (mμ) ($\varepsilon \times 10^{-3}$).

[b] Calculated from the spectrum of a mixture with a *cis*-content of 80% (for **1b**) resp. 30% (for **2b**).

As can be expected, the molar extinction coefficients are lower for the *cis* isomers than for the *trans* isomers, but the wavelengths of maxima and minima are essentially the same for both isomers.

The same conclusions hold for **1c** and **2c**, though in these cases the isomer composition could not be evaluated quantitatively.

Experimental

M.ps were determined in a silicone oil bath, and are not corrected. UV spectra were recorded on a Cary Model 15 spectrophotometer (Applied Physics Corp.) or measured on a Zeiss model PMQ II instru-

TABLE 3. PREPARATION OF POLYENYL-SUBSTITUTED FURANS AND THIOPHENES

Compound	From[a]	Method[b]	Yield[c]	Bp.	Analysis		UV spectrum[d]
					Calc.	Found	
1b[e, f]	**3a**	A	20%	54–55°/11 mm	C, 79·97 H, 6·71	80·1, 80·4 6·8, 6·9	306 (21·4), 292·5 (27·4), 282 (21·4)
1b[g]	**4a**	B	51%	54°/11 mm		—	306 (28·3), 292 (35·7), 282 (26·3)
1c	**4a**	B	28%	77°/2·5 mm	C, 82·16 H, 6·89	82·1, 82·1 6·9, 6·9	334 (45·8), 318 (51·8), 305 (35·5), 230 (11·8)
1c[g]	**5a**	B	45%	mp. 45°		—	336 (49·2), 319·5 (53·8), 307 (36·0), 230 (10·2)
1c	**3a**	B	40%	75°/2mm		—	335·5 (42·8), 319·5 (47·9), 307 (35·5), 230 (12·4)
1d[h]	**6a**	A	14%	42–44°/11 mm	C, 79·97 H, 6·71	79·8, 79·5 6·8, 6·8	318 (11·5) (sh), 312 (18·0), 302 (20·2), 298 (20·9), 290 (16·9)
1e[h, i]	**6a**	A	ca. 1%	84°/0·32 mm	C, 83·69 H, 7·02	83·9 7·0	371 (25·5), 352 (30·6), 336 (22·9), 256 (37·0), 248 (38·6)
1f[j]	**6a**	C	—	—		—	466 (0·10), 418 (0·34), 395 (0·41), 375 (0·31), 296 (1·12), 287 (1·16), 240 (0·30)
2a[k]	**3b**	B	40%	60°/41 mm		—	275 (10·1)
2b[g, l]	**4b**	B	38%	84°/12 mm	C, 70·55 H, 5·92	70·9, 70·9 5·8, 5·9	304 (22·7), 216 (14·0)
2b[m]	**3b**	B	16%	82°/11 mm		—	304 (20·2), 217 (13·4)
2c	**3b**	B	20%	90°/2 mm	C, 74·02 H, 6·21	74·5, 74·8 6·3, 6·2	344 (26·3), 330 (34·6), 318 (28·1) (sh), 244 (17·6)
2c	**4b**	B	10%	66°/0·2 mm		—	345 (22·9), 330 (29·4), 318 (23·7), 246 (12·4)
2c[g]	**5b**	B	34%	mp. 78–79°		—	345 (28·0), 330 (35·4), 318 (28·5), 245 (14·9)
2d	**6b**	C	30%	45°/1·7 mm	C, 70·55 H, 5·92	70·5, 70·9 5·9, 5·9	316 (16·9), 217 (14·2), 212 (14·8)
2e	**6b**	C	ca. 1%	128°/0·2 mm	C, 76·54 H, 6·41	78·1, 78·4 6·5, 6·4	381 (16·5) (sh), 364 (22·9), 350 (19·5) (sh), 258 (21·4), 251 (19·0)
2f[n]	**6b**	C	—	—		—	422 (0·32), 400 (0·47), 379 (0·39), 333 (0·21).

[a] Starting material (aldehyde).

[b] A, B, C: see examples.

[c] Yield after distillation.

[d] Presented as λ_{max} (mμ) ($\varepsilon \times 10^{-3}$). Solvents were isooctane or cyclohexane.

[e] n_D^{20} 1·5826. Lit.[47a]: b.p. 110–115° (20 mm), n_D^{20} 1·5360; lit.[47b] b.p. 105–110° (20 mm), n_D^{20} 1·535. These literature reports concern preparations of **2b** by acid-catalyzed dehydration of 1-(2-furyl)buten-1-ol-3. They probably refer to recovered starting material. Under the reaction conditions mentioned by these authors we could not find any spectroscopic evidence for the formation of **2b** from 1-(2-furyl)buten-1-ol-3.[48]

[f] Contains 80% of the *cis*-isomer.

[g] All-*trans* compound.

[h] Reaction time 16 hr at 60°.

[i] Two other attempted combustion analyses experiments failed, due to an explosive reaction of the compound with pure oxygen.

[j] Optical densities given (concentration unknown). When this solution was allowed to stand for 24 hr much polymeric product precipitated, and the 466 mμ absorption band decreased 6-fold in intensity relative to the main high wavelength band at 418, 395 and 375 mμ. Probably the 466 mμ absorption is caused by minor amounts of stereoisomers.

[k] Lit.[49a]: b.p. 65·5–66·5° (48 mm); lit.[49b] λ_{max} 272 mμ.

[l] Lit.[48]: b.p. 73° (0·4 mm), λ_{max} 307 (22·0) in EtOH.

[m] Contains 30% of the *cis*-isomer.

[n] Optical densities given (concentration unknown). The short wavelength part of this spectrum is uncertain.

ment, using cyclohexane or 2,2,4-trimethylpentane (isooctane) as solvents. NMR spectra were taken on a Varian A-60 instrument in CCl_4 sols, with TMS as internal standard. IR spectra were measured with a Unicam SP 200 spectrophotometer. Microanalyses were performed in the Analytical Department of this laboratory, under the supervision of Mr. W. M. Hazenberg.

The NMR data are presented as chemical shifts in ppm, expressed on the tau-scale ($\tau_{TMS} = 10$), followed by, respectively, a designation of the multiplicity of the signal (s = singlet, d = doublet, m = multiplet), the relative area of the signal, the coupling constants involved, and the assignment of the signal.

The UV data are given as wavelengths of the maxima, followed by the value of $\varepsilon \times 10^{-3}$ (ε expressed in 1 mol^{-1} cm^{-1}).

For the preparation of the aldehydes 3-(2-furyl)propenal[38] (**4a**), 5-(2-furyl)-2,4-pentadienal[39] (**5a**), thiophene-2-carboxaldehyde[40] (**3b**), 3-(2-thienyl)propenal[41] (**4b**), thiophene-2,5-dicarboxaldehyde,[42] and the phosphonium salts methyl- and allyltriphenylphosphonium bromide[43] (**8** and **9**) literature reports were followed.

5-(2-Thienyl)-2,4-pentadienal (**5b**). This compound has been described by Miller and Nord,[44] but we could not reproduce their synthesis. Instead, **5b** was prepared, following the method for the furan analogue **5a**, by condensation of thiophene-2-carboxaldehyde with 2 moles of acetaldehyde.[39] The best results were obtained by carrying out the condensation in 40% aqueous EtOH. **5b** was obtained in 13% yield as yellow crystals: m.p. 32–34° (lit.[44] 44–45°); NMR 0·40 (d, 1, $J = 8$ Hz, -CHO), 3·85 (dd, 1, $J_{trans} = 15$ Hz, $J = 8$ Hz, =CH—CHO), 2·60–3·30 (m, 6, other protons); UV 340 (39·0), 239 (11·1); in 96% EtOH λ_{max}351 mμ. (Found: C, 65·8, 65·6; H, 4·9, 4·9; S, 19·5, 19·4. Calc. for C_9H_8SO: C, 65·82; H, 4·91; S, 19·53).

5-Hydroxymethylfurfural (**7**). An aqueous soln (1·5 l.) of 500 g sucrose and 2·5 g anhyd oxalic acid was heated in an autoclave for 2·5 hr at 125–130° and allowed to cool down. The reaction mixture was worked up as described by Haworth and Jones[22] to give 59 g red-brown liquid product (lit.[22] 80 g) which was not distilled. The IR spectrum was identical with literature data.[45]

Furan-2,5-dicarboxaldehyde (**6a**). A mixture of 85 ml of dry pyridine and 9·34 g (74·1 mmoles) of **7** was cooled to 0° in an icebath.[21] Then 3·37 g (85 mmoles) of lead tetraacetate was added with stirring, causing an initial temp rise to ca. 20°. After 10 min the icebath was removed and stirring was continued for 3 hr. During this period the temp rose to 35°, and dropped to room temp gradually thereafter. The brown reaction mixture was poured into 200 ml of ice water and acidified with 18% HCl, while the temp was kept below 20° by adding ice. The resulting suspension was extracted with $CHCl_3$. The extract was washed with water and $NaHCO_3$, dried ($MgSO_4$) and evaporated to give 7·6 g of a tan solid. This crude product was purified by two sublimations (bath temp 70–100°, 0·1–0·2 mm) and recrystallized twice (CCl_4) to give 3·4 g (27 mmoles, 37%) of **6a**, white leaflets, mp 110–112° (lit.[20] 109–110°); NMR 2·44 (s, 2, ringprotons), 0·12 (s, 2, CHO); UV 291·5 (25·1), 280·5 (25·4), 270 (15·5) (sh); IR 1680 cm^{-1} (C=O). (Found: C, 58·2, 58·4; H, 3·3, 3·2. Calc. for $C_6H_4O_3$: C, 58·07; H, 3·25%).

2,4-Pentadienyl-triphenylphosphonium bromide (**10**). A mixture of 6·6 g (45 mmoles) of 1-bromo-2,4-pentadiene[24] and 11 g (42 mmoles) of triphenylphosphine in 18 ml of benzene was allowed to stand overnight at room temp and refluxed for 30 min. The white ppt was filtered, washed with hot benzene and dried to give 14 g (34 mmoles, 82%) of **10** which was recrystallized from n-butanol or precipitated from a $CHCl_3$ soln with ether: m.p. 217–218°. (Found: Br, 20·6. Calc. for $C_{23}H_{22}PBr$: Br, 19·52%).

2-Vinylfuran (**1a**) was prepared according to Paul[19a] by condensation of furfural and malonic acid, followed by decarboxylation, yield 15%; b.p. 99–100° (lit.[19a–c] 98–99°); n_D^{20} 1·5038 (lit.[19b] 1·4880, lit.[19c] 1·5007); NMR 2·72 (m, 1, 5-furyl-H), 3·8 (m, 2, other ring protons), 3·52 (dd, 1, -*CH*=CH_2, $J_{cis} = 11$ Hz, $J_{trans} = 17$ Hz), 4·35 (dd, 1, $J_{trans} = 17$ Hz, $J_{gem} = 2$ Hz, -CH=C*H*H), 4·90 (dd, 1, $J_{cis} = 11$ Hz, $J_{gem} = 2$ Hz, -CH=C*H*H); UV 272·5 (13·9), 261·5 (18·8), 253 (sh) (15) (lit.[46a] 260·5 (9·3) (no solvent specified), lit.[46b] 266 (6·35) ($CHCl_3$)).

Wittig reactions

In the preparation of **1b-f** and **2a-f** by the Wittig reaction a few standard methods were followed, with minor variations in reaction time and amounts of starting material. In Table 3 the data concerning these preparations are summarized. The three standard methods A, B and C are each illustrated below with an example. More detailed information concerning the preparation of **1a-f** is given in Ref. 1.

All Wittig reactions, including work up and isolation of the products, were carried out in a rigorously maintained N_2 atm.

Method A

2-(1,3-Butadienyl)furan (**1b**, cis-trans *mixture*). To a cooled soln of methylsulfinyl carbanion[28] (generated from 25 ml of DMSO and 2·64 g (55 mmoles) of NaH) was added by means of a syringe a warm soln of 21·1 g (55 mmoles) of **9** in 50 ml DMSO. After stirring for 15 min 4·80 g (50 mmoles) of **3a** was added. The mixture turned brown at once, and the temp rose to 50°. After 15 min the mixture was poured into 100 ml water and the resulting thick brown suspension extracted with pentane. The extract was washed with 50 % aqueous DMSO and brine, and dried ($MgSO_4$). Chromatography of this soln over a column of 40 g of silica gel and elution with 250 ml of pentane gave a soln, which was concentrated and distilled to give 1·18 g (10 mmoles, 20 %) of **1b**.

Method B

2-(1,3-*Butadienyl)furan* (**1b**, trans). To a mixture of 7·10 g (58·2 mmoles) of **4a** and 27·6 g (77 mmoles) of **8** in 150 ml abs ether was added 3·36 g (62 mmoles) NaOMe. The mixture was stirred for 2 hr, refluxed for 30 min and cooled to room temp. To the resulting cream coloured suspension 100 ml water was added, followed by 100 ml pentane. After stirring for 10 min the organic layer was separated and the aqueous layer extracted twice with 100 ml pentane. The combined organic layers, from which much triphenylphosphine oxide had been precipitated by the dilution of ether with pentane, was washed with water and brine, and dried ($MgSO_4$). Evaporation of the solvent in a rotating evaporator gave a yellow oil, which was taken up in 150 ml pentane and chromatographed on a column of silica gel, 20 cm high, 2 cm dia. After elution with 400 ml pentane, no more product came off the column, as measured by UV spectroscopy. A yellow band remained on the column. The column as a whole turned slowly dark, due to decomposition of the product. The eluate was concentrated and the remaining liquid distilled to give 3·57 g (29·7 mmoles, 51 %) of *trans*-**1b**.

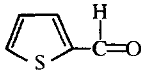
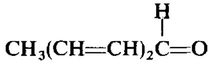
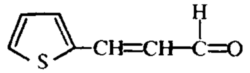
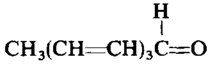
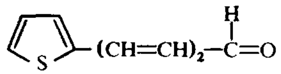
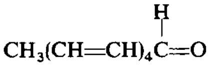
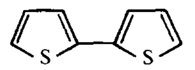
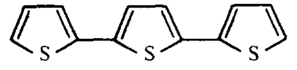
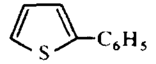
Method C

2,5-*Divinylthiophene* (**2d**). A mixture of 43·0 g (123 mmoles) of **8**, 6·5 g (120 mmoles) of NaOMe and 200 ml of 1,2-dimethoxyethane was stirred for 2 hr at room temp and 1 hr at 60°. To this was added a soln of 8·4 g (59 mmoles) of **6b** in 100 ml 1,2-dimethoxyethane during 30 min. The mixture was heated at 50–60° for 2 hr, cooled down, diluted with 800 ml water and extracted with pentane. After washing with water this extract was dried ($MgSO_4$), evaporated, chromatographed in hexane over neutral alumina, and distilled to give 2·5 g (18 mmoles, 30 %) of **2d**.

Appendix

Some literature data concerning spectra of thiophene derivatives with extended conjugation in the 2-position, and corresponding linear polyenic substances with the same total number of double bonds.

TABLE 4. POSITION OF LONGEST WAVELENGTH ABSORPTION BAND mμ[a]

	285^b	 $CH_3(CH{=}CH)_2\overset{H}{C}{=}O$	270^c
	320^d	 $CH_3(CH{=}CH)_3\overset{H}{C}{=}O$	316^c
	351^e	 $CH_3(CH{=}CH)_4\overset{H}{C}{=}O$	351^f
	$301^{g,h}$	$H(CH{=}CH)_4H$	$304^{h,i,j}$
	$350^{g,h}$	$H(CH{=}CH)_6H$	$364^{h,i,j}$
	282^k	$H(CH{=}CH)_2{-}C_6H_5$	289^l

[a] Solvent ethanol, unless specified otherwise.

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