

## PREPARATION AND STEREOCHEMISTRY OF PENTADIENE DERIVATIVES OF FURAN

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Synthesis of alkyl 5-(5-X-2-furyl)-3-(2-furyl)-2,4-pentadienoates is described. Their stereochemistry was studied and the UV, IR and  $^1\text{H}$  NMR spectra interpreted.

In our previous communications<sup>1-3</sup> we described the preparation of ethyl 4-bromo-3-(2-furyl)-2-butenolate and its reactions with nucleophilic reagents. In the present study the product, arising by reaction of the starting ester with triphenylphosphine, was utilized for preparation of substituted pentadienoates by the Wittig reaction<sup>4-6</sup> (Scheme 1).

The reaction was carried out in methanol with sodium methoxide as the base and its course depended significantly on the way the reaction components were added. Optimum yields were achieved when both components were added simultaneously and the reaction was carried out at 20°C for 1 h. This procedure afforded the furyl-substituted 2,4-pentadienoates as approximately 1:2 : 1 mixtures of *E* and *Z* isomers at the double bond formed. In some cases, the Wittig reaction of 3-ethoxycarbonyl-2-(3-furyl)-2-propenyltriphenylphosphonium bromide with 5-substituted 2-furaldehydes was accompanied by transesterification<sup>7</sup> the extent of which depended on reactivity of the furaldehyde employed.

The strongest bands in the IR spectra of the obtained compounds are due to the ester carbonyl stretching vibrations at 1 695–1 710  $\text{cm}^{-1}$ . In the region 1 595 to 1 610  $\text{cm}^{-1}$  and 1 620–1 630  $\text{cm}^{-1}$  two medium bands are present which are ascribed to stretching vibrations of conjugated double bonds. The characteristic band of the COC furan vibration was situated at 1 000–1 010  $\text{cm}^{-1}$  and the band at around 880  $\text{cm}^{-1}$  was assigned to out-of-plane deformation vibrations of the furan ring<sup>8</sup>.

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Two absorption maxima due to  $\pi-\pi^*$  transition at 270 nm and 330 nm are present in the electronic spectra. Structure of the synthesized compounds was determined first of all by  $^1\text{H NMR}$  spectroscopy. The esters of 5-(5-X-2-furyl)-3-

TABLE I  
Physical constants of the stereoisomeric pairs I–VII

Compound	Formula (mol.wt.)	M.p., °C yield, %	Calculated/Found			
			% C	% H	% N	% Br
<i>I E</i>	$\text{C}_{15}\text{H}_{14}\text{O}_4$ (258.3)	oil	69.70	5.46	—	—
		24.0	69.62	5.37	—	—
<i>I Z</i>	$\text{C}_{15}\text{H}_{14}\text{O}_4$ (258.3)	oil	69.70	5.46	—	—
		20.0	69.03	5.39	—	—
<i>II E</i>	$\text{C}_{15}\text{H}_{14}\text{O}_4$ (258.3)	oil	69.70	5.46	—	—
		30.0	70.39	5.42	—	—
<i>II Z</i>	$\text{C}_{15}\text{H}_{14}\text{O}_4$ (258.3)	oil	69.70	5.46	—	—
		27.0	70.26	5.40	—	—
<i>III E</i>	$\text{C}_{15}\text{H}_{13}\text{NO}_6$ (303.3)	105–106	59.36	4.32	4.61	—
		32.0	59.40	4.30	4.64	—
<i>III Z</i>	$\text{C}_{15}\text{H}_{13}\text{NO}_6$ (303.3)	86–87	59.36	4.32	4.61	—
		30.0	59.23	4.28	4.59	—
<i>IV E</i>	$\text{C}_{14}\text{H}_{11}\text{BrO}_4$ (324.0)	oil	51.85	4.04	—	24.35
		23.0	51.97	4.01	—	24.42
<i>IV Z</i>	$\text{C}_{14}\text{H}_{11}\text{BrO}_4$ (324.0)	oil	51.85	4.04	—	24.35
		20.0	51.34	4.00	—	24.51
<i>VE<sup>a</sup></i>	$\text{C}_{14}\text{H}_{10}\text{Br}_2\text{O}_4$ (392.1)	oil	42.85	2.57	—	40.29
		36.0	42.39	2.45	—	40.20
<i>VZ<sup>a</sup></i>	$\text{C}_{14}\text{H}_{10}\text{Br}_2\text{O}_4$ (392.1)	oil	42.85	2.57	—	40.29
		30.0	42.73	2.40	—	40.18
<i>VI E</i>	$\text{C}_{16}\text{H}_{16}\text{O}_4$ (274.1)	oil	70.04	5.88	—	—
		33.0	69.85	5.79	—	—
<i>VI Z</i>	$\text{C}_{16}\text{H}_{16}\text{O}_4$ (274.1)	oil	70.04	5.88	—	—
		29.0	69.27	6.82	—	—
<i>VII E</i>	$\text{C}_{14}\text{H}_{11}\text{NO}_6$ (257.1)	110–111	65.35	4.31	5.45	—
		15.0	65.47	4.25	5.40	—
<i>VII Z</i>	$\text{C}_{14}\text{H}_{11}\text{NO}_6$ (257.1)	86–87	65.35	4.31	5.45	—
		11.0	65.29	4.29	5.63	—

<sup>a</sup> 4,5-Dibromo derivative.

-(2-furyl)-2,4-pentadienoic acid contain two double bonds, each of which is capable of geometric isomerism. The configuration of the isomers was determined by comparison of the calculated and observed chemical shifts of olefinic protons. The calculation was performed according to an additive relationship<sup>9</sup>, where furan ring increments were substituted by those for an aromatic system.

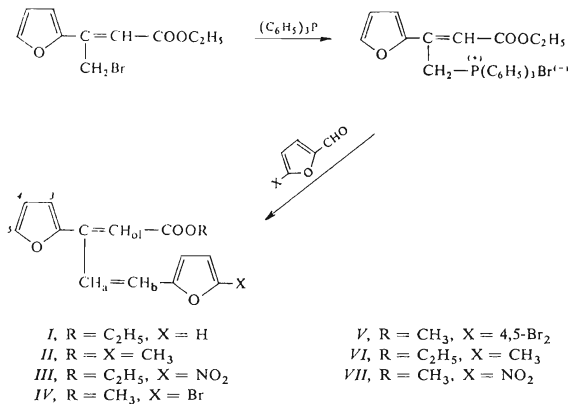
Since reactions leading to the pentadienoates do not involve the double bond linking the ethoxycarbonyl group to the furan nucleus, this double bond has the same configuration (*E*) as in the starting 3-(2-furyl)-2-butenate<sup>10</sup>.

On the other hand, the Wittig reaction gave a mixture of *E* and *Z* isomers at the double bond arising in the reaction. Configuration of this bond was determined from the coupling constants  $^3J(\text{H}_a\text{H}_b)$ , which for the *E* isomers are 16.3–16.7 Hz. However, it was not possible to estimate this coupling constants for the *Z* isomers

TABLE II  
Wavenumbers (in  $\text{cm}^{-1}$ ) of infrared bands (in chloroform)

Compound	$\delta(\text{C—H})$	$\nu(\text{C=O})$	$\nu(\text{C=C})$	$\nu(\text{C=C})$	$\nu(\text{COC})$	$\nu(\text{fur})$	$\nu(\text{CH})$	Other bands
<i>I E</i>	870	1 703	1 600	1 620	1 273	1 000	2 927	—
<i>I Z</i>	869	1 702	1 600	1 620	1 273	1 000	2 924	—
<i>II E</i>	850	1 701	1 600	1 622	1 275	1 005	2 930	1 400 <sup>a</sup>
<i>II Z</i>	870	1 705	1 600	1 624	1 271	1 004	2 931	1 400 <sup>a</sup>
<i>III E</i>	860	1 700	1 598	1 627	1 276	1 002	2 932	1 351 <sup>b</sup>
<i>III Z</i>	862	1 700	1 598	1 627	1 274	1 000	2 924	1 481 <sup>b</sup> 1 351 <sup>b</sup>
<i>IV E</i>	880	1 707	1 610	1 630	1 278	1 005	2 927	1 482 <sup>c</sup>
<i>IV Z</i>	880	1 705	1 610	1 630	1 277	1 006	2 930	—
<i>V E</i>	866	1 702	1 595	1 620	1 281	1 003	2 930	—
<i>V Z</i>	870	1 705	1 600	1 623	1 280	1 008	2 931	—
<i>VI E</i>	860	1 695	1 598	1 629	1 282	1 005	2 942	1 373 <sup>a</sup>
<i>VI Z</i>	870	1 605	1 602	1 629	1 285	1 010	2 932	1 375 <sup>a</sup>
<i>VII E</i>	864	1 702	1 600	1 629	1 278	1 004	2 935	1 352 <sup>b</sup> 1 481 <sup>c</sup>
<i>VII Z</i>	862	1 702	1 600	1 629	1 276	1 000	2 927	1 351 <sup>b</sup> 1 484 <sup>c</sup>

<sup>a</sup>  $\delta(\text{CH}_3)$ , <sup>b</sup>  $\nu_s(\text{NO}_2)$ , <sup>c</sup>  $\nu_{as}(\text{NO}_2)$ .



SCHEME I

TABLE III  
 UV Spectral data ( $\lambda$  in nm; measured in methanol)

Compound	$\lambda_{\text{max}}$	(log $\epsilon$ )	$\lambda_{\text{max}}$	(log $\epsilon$ )
<i>I E</i>	278	(4.31)	321	(4.39)
<i>I Z</i>	265	(4.25)	312	(4.50)
<i>II E</i>	278	(4.33)	357	(4.38)
<i>II Z</i>	278	(4.33)	315	(4.34)
<i>III E</i>	318	(4.21)	365	(4.15)
<i>III Z</i>	312	(4.35)	356	(4.18)
<i>IV E</i>	278	(4.42)	319	(4.49)
<i>IV Z</i>	265	(4.38)	306	(4.24)
<i>VE</i>	282	(4.33)	326	(4.40)
<i>V Z</i>	271	(4.27)	313	(4.31)
<i>VI E</i>	320	(4.25)	366	(4.20)
<i>VI Z</i>	312	(4.36)	356	(4.26)
<i>VII E</i>	276	(4.41)	360	(4.40)
<i>VII Z</i>	276	(4.42)	320	(4.35)

because both the protons in question had the same chemical shift. The olefinic protons were assigned on the basis of the observed and calculated values, using additive increments<sup>9,10</sup>. The mutual arrangement of the double bonds was determined by the long-range interaction between the H<sub>b</sub> and H<sub>01</sub> protons. The observed coupling constant <sup>5</sup>J(H<sub>01</sub>H<sub>b</sub>) is 0.8 Hz, corresponding to an *s-trans* arrangement<sup>11</sup>.

## EXPERIMENTAL

### 3-Ethoxycarbonyl-2-(2-furyl)-2-propenyltriphenylphosphonium Bromide

A solution of triphenylphosphine (2.62 g; 0.01 mol) in benzene was added to a stirred solution of ethyl 4-bromo-3-(2-furyl)-2-butenate (2.59 g; 0.01 mol) in benzene (25 ml). After reflux for 2 h, the separated salt was filtered and washed with benzene; m.p. 106–107°C; yield 89%. For C<sub>28</sub>H<sub>26</sub>BrO<sub>3</sub>P (521.4) calculated: 64.40% C, 4.89% H, 15.32% Br; found: 64.89% C, 4.98% H, 15.50% Br.

TABLE IV

<sup>1</sup>H NMR data (δ, ppm; J, Hz) for alkyl 5-(5-X-2-furyl-3-(2-furyl)-2,4-pentadienoates

Compound	H <sub>3</sub>	H <sub>4</sub> <sup>a</sup>	H <sub>5</sub>	H <sub>01</sub>	H <sub>a</sub> <sup>b</sup>	H <sub>b</sub> <sup>b</sup>	J <sub>H<sub>01</sub>H<sub>b</sub></sub>	H <sub>3'</sub>	H <sub>4'</sub>
<i>IE</i> <sup>c</sup>	6.40 d	6.39 dd	7.50 d	6.18 d	6.58 d	8.06 dd	16.3	6.55 d	6.39 dd
<i>I Z</i> <sup>c</sup>	6.55 d	6.29 dd	7.54 d	6.42 s	6.55 s	6.55 s	—	6.45 d	6.14 dd
<i>II E</i>	6.70 d	6.51 dd	7.48 d	6.12 d	6.87 d	8.01 dd	16.3	6.38 d	5.99 m
<i>II Z</i>	6.46 d	6.19 dd	7.40 d	6.38 s	6.49 s	6.49 s	—	6.05 d	5.81 m
<i>III E</i>	6.69 d	6.51 dd	7.53 d	6.29 d	6.91 d	8.27 dd	16.7	6.69 d	7.34 d
<i>III Z</i>	7.12 d	7.65 dd	7.46 d	6.21 s	6.47 s	6.47 s	—	6.56 d	7.42 d
<i>IV E</i>	6.39 d	6.05 dd	6.51 d	6.37 d	6.83 d	7.23 dd	16.3	6.39 d	6.46 d
<i>IV Z</i>	6.63 d	6.23 dd	7.42 d	6.28 s	6.35 s	6.35 s	—	6.38 d	6.30 d
<i>VE</i> <sup>c</sup>	6.55 d	6.36 dd	7.40 d	6.18 d	6.67 d	8.00 dd	16.4	6.55 s	—
<i>V Z</i> <sup>c</sup>	6.59 d	6.39 dd	7.44 d	6.16 s	6.48 s	6.48 s	—	6.76 s	—
<i>VI E</i>	6.54 d	6.35 dd	6.78 d	6.12 d	6.45 d	8.08 dd	16.2	6.28 d	5.95 d
<i>VI Z</i>	6.31 d	6.23 dd	7.30 d	6.28 d	6.44 s	6.44 s	—	6.31 d	5.78 d
<i>VII E</i>	6.61 d	6.43 dd	7.40 d	6.32 d	6.89 d	8.06 dd	16.2	6.51 d	6.72 d
<i>VII Z</i>	7.08 d	7.36 dd	7.51 d	6.20 s	6.31 s	6.31 s	—	6.50 d	7.42 d

<sup>a</sup> J<sub>34</sub> = 3.2 Hz, J<sub>45</sub> = 1.6 Hz; <sup>b</sup> for *Z*-isomers two-proton singlet; <sup>c</sup> a mixture of methyl and ethyl esters. Other signals: *IE* — 7.44 d (H<sub>5</sub>), 3.77 s (OCH<sub>3</sub>), 4.22 q (OCH<sub>2</sub>), 0.92 t (CH<sub>3</sub>); *I Z* — 7.36 d (H<sub>5</sub>), 3.71 s (OCH<sub>3</sub>), 4.19 q (OCH<sub>2</sub>), 0.91 t (CH<sub>3</sub>); *II E* — 3.76 s (OCH<sub>3</sub>), 2.35 s (CH<sub>3</sub>); *II Z* — 3.69 s (OCH<sub>3</sub>), 2.08 s (CH<sub>3</sub>); *III E* — 4.50 q (OCH<sub>2</sub>), 1.32 t (CH<sub>3</sub>); *III Z* — 4.18 q (OCH<sub>2</sub>), 1.29 t (CH<sub>3</sub>); *IV E* — 3.73 s (OCH<sub>3</sub>); *IV Z* — 3.73 s (OCH<sub>3</sub>); *VE* — 3.69 s (OCH<sub>2</sub>), 4.22 q (OCH<sub>2</sub>).

## Alkyl 5-(5-X-2-Furyl)-3-(2-furyl)-2,4-pentadienoates

A solution of 3-ethoxycarbonyl-2-(2-furyl)-2-propenyltriphenylphosphonium bromide (0.01 mol) and 5-X-furaldehyde (0.01 mol) in methanol was slowly added in a nitrogen atmosphere to a solution of sodium (0.01 mol) in methanol (30 ml). After stirring under nitrogen at room temperature for 2 h, the mixture was taken down and the residue was treated with water (100 ml). The aqueous solution was extracted with benzene ( $3 \times 100$  ml) and the extract was dried and taken down. The obtained mixture of *E* and *Z* isomers was chromatographed on a column of silica gel with benzene as eluant.

## Spectral Measurements

The IR spectra were measured on a double-beam UR-20 (Zeiss, Jena) spectrophotometer in chloroform in the region  $700-3700 \text{ cm}^{-1}$  (0.26 mm cell) or in KBr (2 mg compound per 1 g KBr) in the region  $400-3700 \text{ cm}^{-1}$ . The instrument was calibrated with a  $25 \mu\text{m}$  polystyrene film. The UV spectra were taken on a Specord UV VIS recording spectrophotometer in  $5-7 \cdot 10^{-5}$  mol methanolic solutions; cell thickness 10 mm.  $^1\text{H}$  NMR spectra were obtained with Tesla BS 487 C (80 MHz) instrument in 15% chloroform solutions with tetramethylsilane as internal standard.

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