SYNTHESIS AND PROPERTIES OF STYRYL DERIVATIVES OF 2-FURALDEHYDE

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Reaction of 4-X-benzyltriphenylphosphonium halides with 2-furaldehyde and subsequent Vilsmeier formylation gave 5-(4-X-styryl)-2-furaldehydes (X = H, Cl, Br, CN, NO_2, CH_3, and $COOCH_3$). The UV, IR and ^{1}H-NMR spectra of the prepared substances are discussed and it is demonstrated that the compounds are (*E*) isomers. The UV spectra of 5-styryl-2-furaldehyde have been compared with those of its benzene analogue.

Ethylene derivatives of 2-furaldehyde have been previously prepared by reacting the acidic hydrogen atoms in 5-methyl-2-furaldehyde with 2-furaldehyde to give, under basic conditions, 5-(2-furylvinylene)-2-furaldehyde[1]. It has been found when the conditions of this reaction have been studied that in the presence of potassium or sodium hydroxide products of Cannizaro reaction are produced extensively, and that only small amounts of substituted ethylenes are formed. However, when sodium alkoxide was used as a base the desired ethylene derivatives were formed. Nevertheless, the application of this method for preparing a series of styryl derivatives of 2-furaldehyde was unsuccessful.

In this work we describe syntheses of 5-(4-X-styryl)-2-furaldehydes by reacting corresponding 4-X-benzyltriphenylphosphonium halides with 2-furaldehyde and subsequent Vilsmeier formylation. The method was previously used[2] to prepare 5-styryl-2-furaldehyde. Phosphonium salts were prepared from the corresponding benzyl halide by allowing it to react with triphenylphosphine (Table I). In these conversions sodium methoxide was used as the base to generate phosphorans, and the condensation was performed at 50°C in a nitrogen atmosphere. It follows from works by Wittig and Haag[3] that the yield of the reaction is largely affected by substituents on the benzene ring of the formed ylide: it decreases[4] markedly when electron-withdrawing substituents are present.

The yields obtained in the present work (Table I) are in agreement with that observation. The obtained crude styryl-2-furaldehydes were formylated and the final products were isolated by chromatography on columns of silica gel. In all cases

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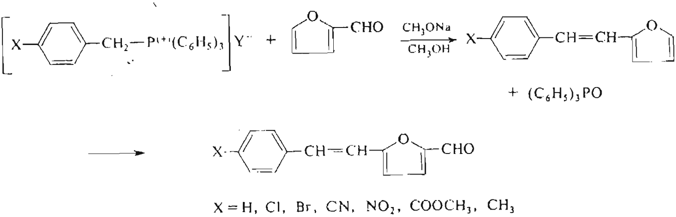
* Part CLIV in the series Furan Derivatives; Part CLIII: This Journal *46*, 506 (1981).

chromatographically pure compounds were obtained. The isomeric purity was confirmed by ^{1}H-NMR spectroscopy which showed that all prepared 5-(4-X-styryl)-2-furaldehydes were (*E*) isomers. Physical constants and other pertinent data for the prepared triphenyl-4-X-benzylphosphonium halides and 5-(4-X-styryl)-2-furaldehydes are in Table I and II.



SCHEME 1

The UV spectra of 5-(4-X-styryl)-2-furaldehydes show three absorption maxima (Table II) the last of which, reflecting the electron transitions of the conjugated

TABLE I
4-X-Benzyltriphenylphosphonium Halides

X	Y	Mol. formula (m.w.)	M.p., °C yield, %
H	Cl	$C_{25}H_{22}ClP$ (388·9)	343—345 80·0
Cl	Cl	$C_{25}H_{21}Cl_2P$ (423·3)	270 85·0
CN	Br	$C_{26}H_{21}BrNP$ (458·3)	347—349 90·0
Br	Br	$C_{25}H_{21}Br_2P$ (512·2)	275 95·7
NO_2	Br	$C_{25}H_{21}BrNO_2P$ (478·9)	287—290 56·0
$COOCH_3$	Br	$C_{27}H_{24}BrO_2P$ (491·3)	255—256 58·5
CH_3	Cl	$C_{26}H_{24}ClP$ (402·9)	248 61·0

TABLE II

5-(4-X-Styryl)-2-furaldehydes

X	Formula (m.w.)	M.p., °C yield, %	Calculated/Found				λ_{max}, nm log ε			$\tilde{\nu}_{(C=O)}$ cm^{-1}
			% C	% H	% N	% Hal				
H	$C_{13}H_{10}O_2$	64	—	—	—	—	234	261	353	1 680
	(198·1)	72					4·11	3·83	4·45	
Cl	$C_{13}H_9ClO_2$	131—133	67·12	3·89	—	15·24	235	265	355, 370s	1 684
	(232·6)	60	67·20	3·75		15·00	4·05	3·90	4·49 4·45	
CN	$C_{14}H_9NO_2$	127—130	75·33	4·06	6·27	—	228	259	360, 375s	1 685
	(223·2)	74	75·20	4·00	6·18		4·06	3·90	4·44 4·33	
Br	$C_{13}H_9BrO_2$	130—131	56·33	3·25	—	28·85	232	264	358, 372s	1 684
	(276·9)	62	56·25	3·19		28·70	4·00	3·92	4·40 4·38	
NO_2[a]	$C_{13}H_9NO_4$	169—171	64·19	3·72	5·75		228	—	378, 394s	1 682
	(243·2)	50	64·05	3·69	5·70		4·28	—	4·56 4·45	
$COOCH_3$	$C_{15}H_{12}O_3$	125—127	80·35	5·35	—	—	232	268	360, 374s	1 684
	(224·0)	58·5	80·18	5·20			4·05	3·90	4·48 4·40	
CH_3	$C_{14}H_{12}O_2$	71—73	79·23	5·69			238	265	361	1 680
	(212·2)	85	79·10	5·70			4·03	3·86	4·43	

[a] $\nu_{s(NO_2)} = 1350$ cm^{-1}, $\tilde{\nu}_{as(NO_2)} = 1530$ cm^{-1}.

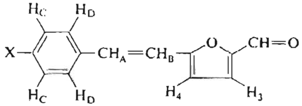
coupling of the benzene and furan rings through an ethylene bridge, is shifted to 378–353 nm. The location of the band depends upon the type of the substituent on the benzene ring. The UV spectrum of the unsubstituted *trans*-2-styrylfuran[2] shows three absorption bands, the K-band appearing at 315 nm. The introduction of an aldehydo group into the furan ring causes a shift of this band by 38 nm.

The band of the aldehydo group appears in the IR spectra at 1680–1685 cm^{-1} and its position is not significantly affected by the nature of the substituent. At 969–973 cm^{-1} deformation stretching $\tilde{\nu}_{(-CH=CH-)}$ bands of the *trans* isomer are present, and those of $\tilde{\nu}_{(C=C)}$ stretchings are located at 1600–1612 cm^{-1}.

The ^{1}H-NMR spectra (Table III) fully confirm the structure of the synthesized substances. The signal of the aldehydo proton appears downfield at ~9·5 ppm, and the protons of the furan ring produce a characteristic doublet showing a coupling constant of 3·6 Hz. The chemical shift of these signals is not much affected by the substituent on the phenyl ring (δ_{ppm} H_4 for the methyl and nitro derivative: 6·48 and 6·65, respectively). The olefinic H_A and H_B protons appear as two doublets, J_{AB} = = 16·3 Hz, the value being characteristic of the arrangement of protons in (*E*) isomers. Their chemical shift largely depends upon the type of substituent at the position 4 of the benzene ring. Aromatic protons constitute an AA'BB' spin system appearing as two broad doublets having a coupling constant of 8·5–9·0 Hz.

TABLE III

^{1}H-NMR Data for 5-(4-X-Styryl)-2-furaldehydes (δ, ppm; J, Hz)



X	H_A[a]	H_B[a]	$J_{A,B}$	H_3[a]	H_4[a]	$J_{3,4}$	H_C[a]	H_D[a]	CHO
H	6·84	7·28	16·4	7·18	6·45	3·7	(7·25—7·56)[b]		9·54
Cl	6·69	7·28	16·6	7·22	6·50	3·6	7·29	7·37	9·56
CN	7·42	7·02	16·3	7·28	6·63	3·7	7·66	7·57	9·62
Br	6·68	7·25	16·3	7·20	6·50	3·6	7·30	7·35	9·57
NO_2	7·41	7·07	16·3	7·28	6·65	3·6	8·24	7·63	9·65
$COOCH_3$	7·48	7·08	16·3	7·28	6·63	3·6	7·30	7·58	9·60
CH_3	6·84	7·35	16·3	7·22	6·48	3·6	7·29	7·38	9·53

[a] Doublet; $J_{C,D}$ = 8·5—9·0 Hz; [b] multiplet of aromatic protons.

EXPERIMENTAL

Electron absorption spectra (200—800 nm) for solutions in methanol were measured with a Specord UV VIS (Zeiss) spectrometer. The IR spectra (700—3 800 cm^{-1}) for chloroform solutions were obtained with a UR 20 instrument calibrated against a 23 μm polystyrene foil The 80 MHz ^1H-NMR spectra for solutions in deuteriochloroform (internal standard tetramethylsilane) were measured at 25°C with a Tesla BS-487 C spectrometer. The proton-signal assignments were done applying the Indor technique.

(4-X-Styryl)-2-furans

A phosphonium salt (0·01 mol) in methanol (20 ml) was added to a solution of sodium (0·01 g-atom) in methanol (20 ml) through which nitrogen had been passed for 10 min, followed by a dropwise addition of 2-furaldehyde (0·01 mol) in methanol (20 ml). The mixture was refluxed for 1·5—2 h, concentrated, and the residue was extracted with hot water. The insoluble material was filtered off, dissolved in chloroform or benzene, the solution was dried (Na_2SO_4), concentrated and the crude product was chromatographed on a column of silica gel using chloroform, benzene or a mixture thereof as a mobile phase.

5-(4-X-Styryl)-2-furaldehydes

A mixture of N,N-dimethylformamide (0·01 mol) and $POCl_3$ (0·01 mol, added dropwise and with stirring at 0°C or below) was stirred for 0·5 h. To the resulting mixture a solution of (4-X-styryl)-2-furan (0 01 mol) in N,N-dimethylformamide (0·02 mol) was added dropwise and with stirring at 0—10°C. The mixture was stirred at room temperature for 1 h, and then for 2—3 h at 70°C. Ice-cold water was added, the mixture was neutralized with sodium carbonate and left overnight. The separated product was filtered off and crystallized or purified by chromatography. When no product had separated, the mixture was extracted with ether, the ethereal solution was dried (Na_2SO_4), concentrated and the crude product was purified as described above.

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