Synthesis and UV and IR Spectroscopic Properties of Some *cis*- and *trans*-2-Styrylthiophenes

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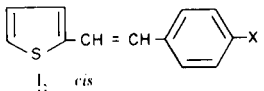
In connection with our research on heterocyclic pentatomic compounds (1) and on the steric course of the Wittig reaction (2), we wish to report the synthesis and uv and ir spectral data of some 2-styrylthiophenes in both *cis*(I) and *trans*(II) forms:



I, *cis*
II, *trans*
X = H, CH_3, Cl, NO_2

Although there are many literature methods for the synthesis of 1,2-diaryl-substituted ethylenes (3-9), the preparation of the styryl heterocyclic compounds (I and II) here reported has been accomplished from a Wittig reaction (10) involving the apposite benzyltriphenylphosphonium chloride and 2-thiophenecarboxaldehyde.

For the ylid generation we preferred the alkoxide method, which in absence of side reactions was found to be more practical and immediate.

In all cases, mixtures of the I and II isomers were obtained in a ratio of about 1:1.5 and their separation was carried out by column chromatography on alumina (see Experimental).

The structure of the *cis*- and *trans*-styrylthiophenes was confirmed by the determination of their uv and ir spectra (see Table I).

The *cis* isomers (I) were also prepared by decarboxylation of the corresponding *cis*-α-phenyl-β-(2-thienyl)acrylic acids (III) whose configuration has been assigned by uv, ir, and nmr spectroscopy (11). Moreover, the compounds I, obtained by decarboxylation, were isomerized to the *trans* isomers with iodine in nitrobenzene (see scheme) in order to compare them with the same stereoisomers obtained from the Wittig reaction.

We have found that the styrylthiophenes prepared by two different methods have the same physical properties and their spectra are coincident.

The uv absorption maxima of the 2-styrylthiophenes examined are reported in Table I. All compounds in both *cis* (I) and *trans* (II) forms, show two main absorption zones: the first at about 230 mμ is not greatly affected by the presence of the heterocyclic ring and is in the same spectral region of the parent stilbenes; the second (K-band) is generally shifted towards longer wavelengths in comparison with that of the corresponding stilbenes (*trans*-stilbene λ max = 290 mμ and *trans*-2-styrylthiophene λ max = 325 mμ).

The spectra of 4′-substituted 2-styrylthiophenes, apart from those of the nitroderivatives, are practically similar to those of the unsubstituted compounds. By a comparison of the spectral data of the *cis* and *trans* isomers it can be observed that the K-bands of the formers are always located at lower wavelengths (18-36 mμ) and show also

Scheme

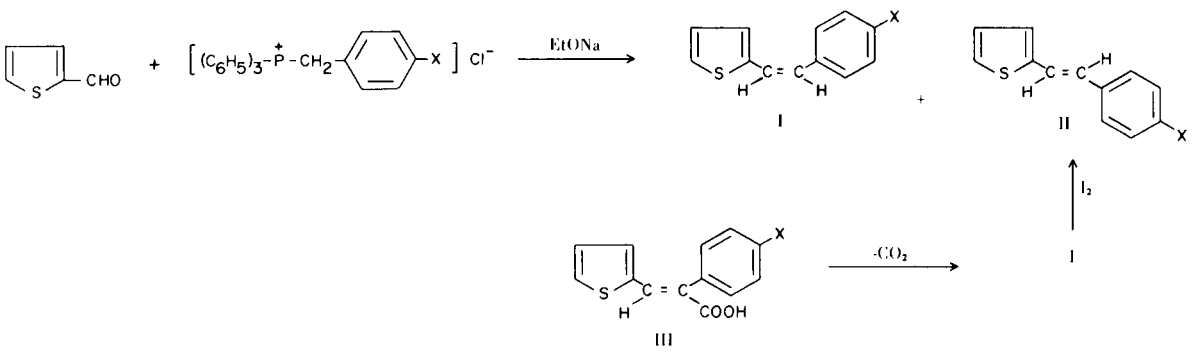


TABLE I

Uv and Ir Spectral Data of *cis*- and *trans*-2-Styrylthiophenes

X	Ultraviolet λ max mμ (log ε) *cis*	*trans*	Δ λ (a)	Infrared cm^{-1} ν CH *cis*	ν CH *trans*
H	233 (4.01) (b)	230 (3.98) (c) 270i (3.71) (c)		1395	948 (c)
	290 (3.99) (b)	325 (4.42) (c)	35		
CH_3	237 (4.08)	232 (3.99) (d)		1394	951
	294 (3.99)	327 (4.45) (d)	33		
Cl	240 (4.12)	234 (3.95) 240 (3.96)		1410	951
	292 (4.02)	328 (4.27)	36		
NO_2	269 (4.20)	272 (4.09) (c)		1399	946 (c)
	354 (3.88)	372 (4.21) (c)	18		

(a) Difference between λ *cis* max and the corresponding λ *trans* max at longer wavelength. (b) Ref. 15. Data refer to methanolic solution. (c) A. Arcoria, E. Maccarone, and G. A. Tomaselli, *Spectrochim. Acta*, in press. (d) Ref. 17. i: inflection

lower intensities.

The *cis*- and *trans*-styrylthiophenes I and II were also characterized by comparison of their ir spectra.

The *trans* isomers show strong C-H out of plane bending absorption of the vinyl group in the region 946-951 cm^{-1} (see Table I), this band being absent for the *cis* isomers; for these it was found as being characteristic the band at 1395-1410 cm^{-1}, already reported by N. Sheppard and D. M. Simpson (12) for the *cis*-dialkyl-substituted olefins and attributed to C-H bending in plane.

EXPERIMENTAL

cis- and *trans*-2-Styrylthiophene (I and II, X = H).

To a stirred solution of 7.78 g. (0.02 mole) of benzyltriphenylphosphonium chloride (13) (obtained from benzyl chloride and triphenylphosphine in chloroform) and 2.24 g. (0.02 mole) of 2-thiophenecarboxaldehyde in 20 ml. of ethanol was added a solution of 0.46 g. of sodium in ethanol. After stirring for 30 minutes the reaction mixture was diluted with petroleum ether and the solid collected. Crystallization from ethanol gave 1.8 g. of *trans*-2-styrylthiophene, m.p. 111° (lit. (14) m.p. 111°).

The filtrate in absence of sun light, was concentrated and chromatographed on alumina using petroleum ether as the eluent. Evaporation of the solution and distillation of the residue gave 1.2 g. of *cis*-2-styrylthiophene, b.p. 93°/0.3 mm (lit. (15) b.p. 74°/0.1 mm).

cis- and *trans*-2-(4′-Methylstyryl)thiophene (I and II, X = CH_3).

These compounds were obtained in a *cis*/*trans* ratio of 1:1.3 from equimolar amounts of 4-methylbenzyltriphenylphosphonium chloride (16) and 2-thiophenecarboxaldehyde following the procedure previously described. The *trans*-2-(4′-methylstyryl)thiophene crystallized from ethanol and melted at 115-116° (lit. (17) m.p. 115-116°); the *cis* isomers, after elution with petroleum ether from alumina and distillation, had a boiling point of 103.5°/0.3 mm.

Anal. Calcd. for $C_{13}H_{12}S$: C, 77.95; H, 6.05; S, 16.01. Found (*cis*): C, 77.87; H, 6.01; S, 16.10. Found (*trans*): C, 77.99; H, 6.07; S, 16.00.

cis- and *trans*-2-(4′-Chlorostyryl)thiophene (I and II, X = Cl).

These compounds were obtained as above by a Wittig reaction from equimolar amounts of 4-chlorobenzyltriphenylphosphonium chloride (18) and 2-thiophenecarboxaldehyde.

The *trans* compound which separated was crystallized from ethanol, m.p. 137° (lit. (19) m.p. 137°).

The residual oil after elution with petroleum ether from alumina and distillation gave the *cis* isomer, b.p. 114.5°/0.25 mm (*cis*/*trans* ratio 1:2).

Anal. Calcd. for $C_{12}H_9ClS$: C, 65.30; H, 4.11; S, 14.52. Found (*cis*): C, 65.22; H, 4.14; S, 14.61. Found (*trans*): C, 65.28; H, 4.08; S, 14.57.

cis- and *trans*-2-(4′-Nitrostyryl)thiophene (I and II, X = NO_2).

The reaction between 4-nitrobenzyltriphenylphosphonium chloride (20) and 2-thiophenecarboxaldehyde affords a mixture of *cis*- and *trans*-2-(4′-nitrostyryl)thiophene in a ratio of about 1:1.5.

The *trans* compound which first precipitated, was filtered off and crystallized from ethanol, m.p. 173-174° (lit. (19) m.p. 174°).

The residual solution, chromatographed on alumina, (using petroleum ether-benzene 2:1 as eluent) under red light, gave after concentration, the *cis* isomer, m.p. 68°, from ligroin.

Anal. Calcd. for $C_{12}H_9NO_2S$: C, 62.32; H, 3.92; S, 13.86. Found (*cis*): C, 62.40; H, 3.99; S, 13.91. Found (*trans*): C, 62.35; H, 3.95; S, 13.83.

Decarboxylation of *cis*-α-phenyl-β-(2-thienyl)acrylic Acids.

cis-α-Phenyl-β-(2-thienyl)acrylic acid (3 g.) obtained by a Perkin reaction from the corresponding phenylacetic acid and 2-thiophenecarboxaldehyde (11), were dissolved in 30 ml. of quinoline and 0.4 g. of copper chromite was added.

The solution was boiled for about 1 hour and after cooling was acidified with dilute hydrochloric acid and extracted with ether. Evaporation of the ethereal solution and distillation of the residue gave the *cis*-diarylethylene. The yields were about 60%.

The *cis* compounds prepared by this procedure were all identical to those obtained from the Wittig reaction.

Isomerization.

cis-Diarylethylene (0.5 g.) obtained by decarboxylation of the corresponding acrylic acid (see above) was boiled with 10 ml. of nitrobenzene in the presence of iodine for 30 minutes. After evaporation of the solvent the crude solid was collected and purified by crystallization from ethanol.

The *trans*-styrylthiophenes prepared in this manner had the same physical constants (m.p. and mixed m.p.) as those obtained by the Wittig reaction.

Uv Spectra.

Uv spectra were obtained with a Hitachi-Perkin Elmer model EPS-3T spectrometer, using about 1.10^{-5} molar solutions in 95% ethanol.

Ir Spectra.

Ir spectra were determined in carbon tetrachloride using a Perkin-Elmer model 237 spectrometer.

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