CROATICA CHEMICA ACTA CCACAA **62** (1) 81—87 (1989)

YU ISSN 0011-1643
CCA-1842 UDC 544.62
Note

Synthesis and Spectroscopic Properties of Some New *cis*- and *trans*-1-(2-Furyl)-2-(*o*-tolyl)ethenes

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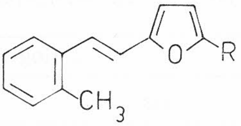
Received November 9, 1987

New *o*-methyl substituted furylphenylethenes were prepared by Wittig reaction and the *cis*- and *trans*-isomers separated by column chromatography. The isomers were characterized by their UV, ^{1}H and ^{13}C NMR spectral data.

As a part of our interest[1] in the chemistry of *o*-substituted heterocyclic analogues of stilbene compounds we report herein the synthesis and spectral properties of new *cis*- and *trans*-1-(2-furyl)-2(*o*-tolyl)ethenes (*1*—*5*) which are important because of their photochemical behaviour and as intermediates for the synthesis of various biologically and physiologically active compounds.



cis-, *trans*-
1, R = H; *2*, R = CH_3; *3*, R = Br;
4, R = *p*-Tolyl; *5*, R = *p*-Nitrophenyl

RESULTS AND DISCUSSION

Though several methods for the synthesis of styrylfuranes have been described in the literature,[2-7] the *o*-methyl substituted styrylfurans reported herein (Table I) were prepared by the Wittig reaction, the most convenient synthetic method in this case, involving the *o*-xylyltriphenylphosphonium bromide and the corresponding furancarboxaldehydes in the presence of sodium ethoxide. Isomeric mixtures of *cis*- and *trans*- *1*—*5* were obtained in a very good yield in all cases (see Table I). The isomers were separated by repeated column chromatography on silica gel using petroleum ether as eluent.

The structure of the isomers was determined by their UV, ^{1}H and ^{13}C NMR spectra.

TABLE I

cis- *and* trans-*1-(2-furyl)-2-(*o*-tolyl)ethenes* (1—5)

No.	Isomer	R	*M. p.* °C	Ratio (%)[a] *cis : trans*	Yield[b] (%)	*m/z* (M$^+$)	*Anal.* C	Calcd.: Found: H	(%) N
1	*cis*	H	oil				84.75	6.57	
	trans	H	oil	40 : 60	87	184	84.86	6.87	
2	*cis*	CH_3	oil				84.81	7.12	
	trans	CH_3	49—50	30 : 70	85	198	84.69	7.04	
3	*cis*	Br	oil				59.33	4.21	
	trans	Br	55—56	40 : 60	90	262	59.15	3.92	
4	*cis*	*p*-tolyl	35—36				87.56	6.61	
	trans	*p*-tolyl	98—99	30 : 70	86	274	87.31	6.85	
5	*cis*	*p*-nitrophenyl	84—85				74.74	4.95	4.59
	trans	*p*-nitrophenyl	130—131	20 : 80	76	305	74.84	5.17	4.63

[a] Based on ^{1}H NMR spectrum.
[b] All yields refer to isolated pure products.

UV spectral data demonstrated in Table II show that the furan analogue of 2-methylstilbene (*1*) has a considerable absorption shift towards longer wavelengths in comparison to the corresponding stilbene (*trans*-2-methylstilbene, $\lambda_{max} = 307$ nm) due to the conjugation from the oxygen lone pair through the furan ring. The substituted derivatives of *1* (*2*—*5*) show substituent effects which depend on the electron donating or withdrawing effect of the substituent. They show a bathochromic effect which is specially pronounced in compound *5* due to the extended conjugation by *p*-nitrophenyl group.

TABLE II

UV spectral data of cis- *and* trans-*1-(2-furyl)-2-(*o*-tolyl)ethenes*

No.	R	λ_{max} (log ε) in ethanol	
		cis	*trans*
1	H	230(3.94), 282(4.16)	230(3.98), 243(3.72), 311(4.56), 323(4.55), 338(4.28)
2	CH_3	230(3.90), 287(4.04)	229(3.89), 325(4.34)
3	Br	233(4.05), 288(4.34)	233(3.98), 315(4.58), 329(4.58), 347(4.31)
4	*p*-tolyl	253(4.01), 323(4.30)	238(4.14), 254(4.13), 355(4.49)
5	*p*-nitrophenyl	233(4.03), 300(3.91), 400(4.28)	237(4.20), 313(4.22), 408(4.46)

The ^{1}H NMR spectra of the new compounds are presented in Table III (taken in $CDCl_3$) and Table IV (taken in C_6D_6). They show well resolved patterns of aromatic, ethylenic and furanic hydrogens. The chemical shifts for the ethylenic hydrogens are very close to those found for stiblenes[8] and 1,2-difurylethenes[9]. Depending on the substituent, they appear for the *cis*-

-isomer as a singlet (R=H, CH_3, *p*-tolyl) or as two doublets (R=Br, *p*-nitrophenyl). In the *trans*-isomer the ethylenic hydrogens are shifted downfield in comparison to the *cis*-isomer: one hydrogen appears as a doublet near δ 6.7 while the other is seen as a multiplet of aromatic hydrogens.

TABLE III

^1H NMR spectra of cis- *and* trans-*1-(2-furyl)-2-(*o*-tolyl)ethenes in $CDCl_3$ (δ, TMS)*

No.	R		H_{ar}	H_{et}	H_{fur}	CH_3
1	H	*cis*	7.1—7.4	6.48(s, 2H)	5.90(dd), 6.22(dd)	2.25
		trans	7.1—7.6	6.78(d, 1H)	6.33(dd), 6.42(dd)	2.42
2	CH_3	*cis*	7.0—7.4	6.38(s, 2H)	5.77(s, 2H)	2.15, 2.22
		trans	7.1—7.6	6.70(d, 1H)	5.96(dq), 6.17(d)	2.30, 2.38
3	*Br*	*cis*	7.1—7.4	6.41, 6.51 (AB, 2H)	5.77(d), 6.11(d)	2.24
		trans	7.1—7.7	6.66(d, 1H)	6.27(d), 6.33(d)	2.42
4	*p*-tolyl	*cis*	7.0—7.5	6.47(s, 2H)	6.07(d), 6 42(d)	2.26, 2.28
		trans	7.1—7.7	6.80(d, 1H)	6.42(d), 6.64(d)	2.38, 2.47
5	*p*-nitro-phenyl	*cis*	7.2—8.2	6.45, 6.49 (AB, 2H)	6.19(d), 6.74(d)	2.29
		trans	7.1—8.3	6.81.(d, 1H)	6.51(d), 6.93(d)	2.49

Coupling constants (Hz): $J_{3,4} = 3.4$, $J_{4,5} = 1.8$, $J_{3,5} = 0.5$, $J_{4,Me} = 0.9$, $J_{et} = 12.4$(*cis*), $J_{et} = 16.4$(*trans*).

TABLE IV

^1H NMR spectra of cis- *and* trans-*1-(2-furyl)-2-(*o*-tolyl)ethenes in C_6D_6 (δ, TMS)*

No.	R		H_{ar}	H_{et}	H_{fur}	CH_3
1	H	*cis*	6.9—7.4	6.29, 6.42 (AB 2H)	5.89, 5.90 (AB 2H)	2.10
		trans	6.9—7.5	6.69(d, 1H)	6.08(dd), 6.13(dd)	2.17
2	CH_3	*cis*	6.9—7.5	6.27, 6.44 (AB 2H)	5.62(dq), 5.91(d)	1.89, 2.13
		trans	6.9—7.5	6.72(d, 1H)	5.81(dq), 6.08(d)	2.01, 2.17
3	Br	*cis*	6.9—7.3	6.20(s, 2H)	5.65(d), 5.75(d)	2.03
		trans	6.9—7.4	6.45(d, 1H)	5.79(d), 5.96(d)	2.06
4	*p*-tolyl	*cis*	6.9—7.6	6.36(S, 2H)	6.06(d), 6.28(d)	2.05, 2.15
		trans	7.0—7.7	6.43(d, 1H)	6.19(d), 6.46(d)	2.08, 2.20
5	*p*-nitro-phenyl	*cis*	6.9—7.9	6.23, 6.41 (AB, 2H)	5.94(d), 6.15(d)	2.10
		trans	7.0—7.9	6.65(d, 1H)	6.08(d), 6.33(d)	2.24

The furan hydrogens[10–16] at C-3 and C-4 are well separated and clearly distinguishable from the other hydrogens. They appear as two doublets ($J = 3.4$ Hz) at δ 5.7—6.7 for the *cis*-isomer or at δ 6.0—6.9 for the *trans*-isomer. It is interesting to note that the *cis*-isomer *2* with the methyl substituent in position 5 of the furan ring shows magnetically equivalent furan hydrogens. These appear as a singlet at δ 5.8 of twice the intensity. Changing the solvent to C_6D_6, the large aromatic solvent induced shift (ASIS) is observed. The same hydrogens become well resolved: the H_3 exhibits a doublet ($J = 3.4$ Hz) whereas the H_4 appears as a double quartet ($J = 3.4$ and 0.9 Hz)[17] thus showing the coupling with methyl hydrogens. In contrast to *cis-2*, the *cis*-compound *1* with no substituent on the furan ring shows two well separated groups of double doublets in deuterochloroform at δ 5.9 and 6.2 (AX case). On the basis of the coupling constants, the lower field signal is assigned to hydrogen at C-4 ($J_{3,4} = 3.4$ and $J_{4,5} = 1.8$ Hz) and the higher field signal to the hydrogen at C-3 ($J_{3,4} = 3.4$ and $J_{3,5} = 0.5$ Hz). However, in deuterobenzene solution the hydrogens at C-3 and C-4 appear as an AB system with strongly enlarged inner peaks hardly distinguishable (δ 5.89 and 5.9). The hydrogen at C-5 is in all cases shifted to the aromatics and it could not be observed. The methyl group of *cis*-isomers is always slightly shifted to the higher field in comparison to that of *trans*-isomers.

TABLE V

Carbon-13 chemical shifts of compounds 1—5 (ppm, $CDCl_3$, TMS)

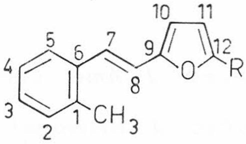
No.	R	isomer	CH_3 (q)	C-1, C-6 (s)	C-8 (d)	C-9, C-12 (s)	C-10, C-11 (d)	C-2, 3, 4, 5(d) C-7(d), C-1^a(s), C-6^a(s) C-phenyl
1	H	*cis*	19.6	136.8 135.5	118.8	151.9 141.0	110.9 108.8	127.1, 127.0, 125.3, 128.3, 129.6
		trans	19,0	135.4 135.5	117.2	153.1 141.6	111.3 108.3	127.2, 124.5, 124.4, 125.9, 130.1
2	CH_3	*cis*	19.6 13.4	137.4 135.8	119.3	152.0 150.7	110.1 107.5	127.2, 125.8, 125.5, 128.7, 129.8
		trans	19.9 13.7	135.6 136.2	117.8	152.1 152.1	109.8 107.8	127.2, 124.8, 123.1, 126.1, 130.5
3	Br	*cis*	19.6	136.6 135.7	118.3	153.3 120.7	111.9 112.9	128.1, 126.1, 125.7, 128.3, 130.0
		trans	19.8	135.5 135.8	116.5	155.5 121.5	110.5 113.3	127.7, 125.4, 124.9, 126.1, 130.5
4	*p*-tolyl	*cis*	19.6 21.0		118.6	159.2 151.4	111.8 105.7	128.6, 126.1, 125.3, 127.6, 129.7, 125.5(s), 136.9(s) 135.7(s), 127.8(s), 129.0(2) 123.5(2)
		trans	19.9 21.3		117.4	153.8 152.8	110.9 106.9	127.4, 134.9, 124.4, 126.2, 130.5, 137.3(s), 136.1(s) 135.8(s), 128.1(s), 129.4(2), 123.9(2)
5	*p*-nitro-phenyl	*cis*	19.8		117.8	153.5 150.1	112.3 110.3	128.4, 127.3, 125.2, 129.1, 129.6, 135.7(s), 136.9(s), 135.5(s), 135.4(s), 123.8(2), 123.2(2)

TABLE VI

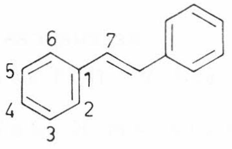
Carbon-13 chemical shifts of trans-*compounds 6—7 (ppm,* $CDCl_3$, *TMS)*

No.	C-1	C-2	C-3	C-4	C-5	C-7	Ref.
6	137.6	126.8	128.9	127.8		129.0	18
7	141.7	108.5	111.4	152.6	114.7		

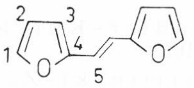
The chemical shifts of the carbon atoms of compounds *1—5* are shown in Table V. The assignments were made on the basis of the signal multiplicities and by comparison with the reported chemical shifts values of stilbenes (*6*)[18] and furans[19–21] using substituent-induced shift increments.[22] To obtain appropriate comparable chemical shifts of furan moiety of compounds *1—5*, the ^{13}C NMR spectrum of 1,2-difurylethene (7) was recorded (Table VI).



1—5



6



7

The spectrum of 7 exhibits five very well recognizable signals: C-1 and C-4 at 141.7(d) and 152.6(s) ppm, C-2 and C-3 at 108.5(d) and 111.4(d) ppm and the ethylenic carbon (C-5) at 114.7(d) ppm. From a brief examination of the values, combined with the literature data[18–22] and the data obtained by the off-resonance technique, many carbons of compounds *1—5* can be unambiguously assigned. It can be seen from the data summarized in Table V that carbons C-10 and C-11 of the furan ring appear in the region between 107—113 ppm and are in good agreement with C-2 and C-3 of compound 7. The signals of C-9 and C-12 are downfield shifted, as expected due to the oxygen atom, and correspond to the signals of C-4 and C-1 in compound 7. While C-9 carbon signal is observed near 150 ppm, the C-12 is more influenced by substituents and its position varies considerably: 140 (R=H), 120 (R=Br), and 150 ppm (R=CH_3 and phenyl substituents). This is in accordance with the calculated values by addition of substituent effects.[22] The signals of ethylenic carbons C-8 are observed close to the furanic C-10 and C-11 but they are easily assigned from their additional splittings[23] in the off-resonance spectra. The C-8 chemical shifts vary a little, being only slightly influenced by substituents R.

EXPERIMENTAL

All melting points are uncorrected. The ^{1}H and ^{13}C NMR spectra were recorded on a JEOL FX-90 Q instrument using $SiMe_4$ as internal standard, in $CDCl_3$ and C_6D_6 solutions. Mass spectral data were obtained on a Varian MAT CH-7 (70 eV) instrument. UV spectra were determined on the Perkin-Elmer double beam spectrophotometer 124. Silica gel (Merck 0.05—0.2 mm) was used for chromatographic separations. Arylsubstituted furancarboxaldehydes were prepared according to the procedure described in literature.[24]

General Procedure for the Preparation of Substituted 1-(2-Furyl)-2-(o-tolyl)ethenes (1—5)

A solution of sodium ethoxide (obtained by dissolving 0.015 mole of sodium in 20 ml absolute ethanol) was added dropwise to a stirred solution of *o*-xylyltriphenylphosphonium bromide (0.01 mole, prepared from *o*-xylylbromide and triphenylphosphine in benzene) and the corresponding aldehyde (0.011 mole) in absolute ethanol (30 ml). The resulting solution was stirred at room temperature overnight. After removal of the solvent under reduced pressure, the residue was worked up by adding water and then extracting with benzene. The benzene extracts were dried ($MgSO_4$) and aveporated to dryness, affording a semisolid residue. The product was extracted with petroleum ether. After evaporation of solvent the reaction mixture was purified and separated by repeated column chromatography on silica gel using petroleum ether as eluent. The first fractions from column chromatography yielded *cis*-isomer and the last fractions *trans*-isomer. The yields, melting points, analytical data and the ratio of *cis-trans*-isomers based on the ^1H NMR spectra are given in Table I.

Acknowledgement. — The financial support of the Republic Fund for Scientific Work of Croatia is gratefully acknowledged. We thank Dr. M. Maksić for critical reading of the manuscript.

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SAŽETAK

Sinteza i spektroskopska svojstva nekih novih *cis-* i *trans*-1-(2-furil)-2-(*o*-tolil)etena

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Wittigovom reakcijom priređeni su novi *o*-metil-supstituirani furilfenileteni, a *cis-* i *trans*-izomeri odijeljeni su kromatografijom na koloni. Izomeri su karakterizirani UV, ^{1}H i ^{13}C spektrima.