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Some 1-(2-furyl)-2-arylethylenes, where the furan nucleus is substituted in position 5 with a methyl or *p*-chlorophenyl group and where the aryl group is phenyl, *p*-nitrophenyl, α -naphthyl or β -naphthyl, have been prepared by the Perkin reaction and subsequent decarboxylation of the acid. The compounds 1-12 were prepared for of photochemistry and photoelectron spectroscopy studies. Their geometrical configurations has been established by ^1H nmr and ir spectra.

J. Heterocyclic Chem., **18**, 193 (1981).

The 1-(2-furyl)-2-arylethylenes are very suitable compounds in order to study the effects of substituents and geometry of the molecule in their excited states (the photochemical behaviour and mass spectrometry fragmentation pattern). Heterocyclic analogues of stilbene-like compounds deserve special attention.

As a part of our continuing interest in the chemistry of furan compounds, the photochemical *cis-trans* isomerizations (1), and photodehydrocyclization (2), some 1-(2-furyl)-2-arylethylenes were reported. This paper describes the preparation of some 1-(2-furyl)-2-arylethylenes by a modified Perkin reaction (3). The geometrical configuration of the compounds which were prepared (Table II), was confirmed by their ir spectra (characteristic "out of plane" C-H deformation vibrations in the region of 1000-800 cm^{-1}) (4) and ^1H nmr spectra (Table III). Until the present research, only a few 1-(2-furyl)-2-arylethylenes have been prepared (5,6).

EXPERIMENTAL

Melting points are uncorrected. The ir spectra were taken on a Perkin-Elmer Infracord model 137 in potassium bromide pellets. The ^1H nmr spectra were taken on a Varian T-60 or a Varian HA-100 spectrometer with TMS as the internal standard. Chemical shifts are given in ppm (δ).

General Procedure.

Perkin Reaction.

A mixture of substituted phenylacetic acid or naphthylacetic acid (7) (0.054 mole), the corresponding 5-substituted furfural (0.064 mole), triethylamine (10 ml.) and acetic anhydride (10 ml.) was heated 1-3 hours at the boiling point. After the reaction was completed, the mixture was cooled, acidified with concentrated hydrochloric acid and extracted with ether. The organic layer was washed with water and the acids re-extracted into 5%

sodium carbonate solution. The alkaline solution of sodium salts was acidified to pH 6 with acetic acid. The precipitated *E*-isomer was filtered off and recrystallized from ethanol. To the filtrate, concentrated hydrochloric acid was added, and an additional crystalline crop consisting of the *Z*-isomer was filtered off and recrystallized from benzene/petroleum ether (Table I).

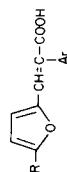
Decarboxylation.

Decarboxylation of the corresponding *E*-acids was accomplished by the known method (8) by heating 5 g. of the requisite acid with 5 g. of Cu-powder in 25 ml. of quinoline (dried over molecular sieves) during 1 hour at the boiling point. The reaction mixture was taken into 50 ml. of ether and washed with 70 ml. of 10% hydrochloric acid. Etheral extracts were separated from the water layer, which was extracted twice with ether. All etheral extracts were collected, washed with water, 10% hydrochloric acid and water and dried over magnesium sulfate. The ether was evaporated and the residue was purified by vacuum distillation, by repeated elution on silica with chloroform, or by crystallization from petroleum ether.

REFERENCES AND NOTES

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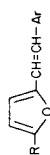
Table I



2-Aryl-3-(5-substituted-2-furyl)acrylic Acids

No.	R	Ar	Stereo isomer	Reaction time [minutes]	Yield [%]	M.p. [°C]	Ir/cm ⁻¹ C=C C=O	Analysis C[%]	Calcd. Found H[%]	¹ H Nmr/δ (ppm) H-ethylenic
I	Methyl	<i>p</i> -Nitro-phenyl	<i>E</i>	60	52.3	210-214	1600 1664	61.54 61.43	4.06 4.25	7.95 (s)
Ia	Methyl	<i>p</i> -Nitro phenyl	<i>Z</i>		18.7	196-198	1588 1670	61.54 61.85	4.06 4.07	7.10 (s)
II	<i>p</i> -Chloro phenyl	Phenyl	<i>E</i>		59.5	208-210	1607 1670	70.27 70.01	4.03 3.97	7.80 (s)
IIa	<i>p</i> -Chloro phenyl	Phenyl	<i>Z</i>	50	2.8	163-166	1580 1680	70.27 69.98	4.03 4.12	6.92 (s)
III	<i>p</i> -Chloro phenyl	<i>p</i> -Nitro-phenyl	<i>E</i>		50.8	217-220	1614 1670	61.71 61.39	3.27 3.54	7.93 (s)
IIIa	<i>p</i> -Chloro phenyl	<i>p</i> -Nitro-phenyl	<i>Z</i>	60	8.6	231-234	1590 1680	61.71 61.92	3.27 3.43	6.95 (s)

Table II

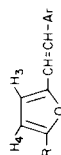


1-(2-furyl)-2-arylethylenes

No.	R	Ar	Yield [%]	M.p. [°C]	B.p. [°C] [mm Hg]	Isomer	Analysis C [%]	Calcd. Found H [%]	Recrystallized from	C=C	Ir/cm ⁻¹ C-H (ethylenic out of plane)
1(a)	H	Phenyl	85		120-125/9	<i>cis</i>	84.76	6.56		1580	698
2	Methyl	Phenyl	80		125-129/10	<i>cis</i>	84.56	6.26		1580	698
3	Methyl	<i>p</i> -Nitro- phenyl	14	78-81		<i>trans</i>	68.18	4.84	petroleum ether	1620	956
4	<i>p</i> -Chloro- phenyl	Phenyl	18.8	108-112		<i>cis</i>	68.33	5.00	petroleum ether	1580	962 697
5	<i>p</i> -Chloro- phenyl	<i>p</i> -Nitro- phenyl	40	72-75		<i>cis</i>	77.27	4.90	petroleum ether	1610	965 698
6	H	α -Naphthyl	12		60-70/10	<i>cis</i>	66.71	4.00	petroleum ether	1580	695
7	H	α -Naphthyl	38.2		180-190/10	<i>trans</i>	87.23	5.50		1580	953
8	H	β -Naphthyl	10.2		60-70/10	<i>cis</i>	87.01	5.54		1585	695
9	H	β -Naphthyl	25.3	90	200/10	<i>trans</i>	87.23	5.50	petroleum ether	1600	962
10	Methyl	α -Naphthyl	87		60-70/10	<i>cis</i>	87.08	5.23		1565	697
11	Methyl	α -Naphthyl	34.6		195-201/12	<i>trans</i>	87.14	6.02		1620	945
12	Methyl	β -Naphthyl	12.5	105-106		<i>trans</i>	87.23	6.22	petroleum ether	1590	958
							87.14	6.31			
							87.27				

(a) The compound was prepared by C. E. Loeder and C. Y. Timmons (5) and S. Fischella, *et al.*, (6).

Table III

¹H Nmr Spectra of 1-(2-Furyl)-2-arylethylenes

No.	R	Ar	Isomer	H ethylenic (a)	H ₃ (a,b)	H ₄ (a,b)	H (aromatics) (a)	H(CH ₃) (a)
1	H	Phenyl	<i>cis</i>	6.38 (s) (c)	6.22 (s) (c)	6.22 (s) (c)	7.17-7.48 (m)	
2	Methyl	Phenyl	<i>cis</i>	6.28 (s) (c)	6.12 (d) (J _{3,4} = 3.5)	5.82 (d) (J _{3,4} = 3.5)	7.13-7.8 (m)	2.2 (s)
3	Methyl	<i>p</i> -Nitro-phenyl	<i>trans</i>	6.9 (s) (c)	6.03 (d) (J _{3,4} = 3.5)	6.37 (d) (J _{3,4} = 3.5)	7.48-8.3 (m)	2.38 (s)
4	<i>p</i> -Chloro-phenyl	<i>p</i> -Nitro-phenyl	<i>cis</i>	unresolved multiplet	6.2-7.8 (m)			
5	<i>p</i> -Chloro-phenyl	<i>p</i> -Nitro-phenyl	<i>cis</i>	6.48 (s) (c)	6.45 (d) (J _{3,4} = 1.8)	6.67 (d) (J _{3,4} = 1.8)	7.1-8.26 (m)	
6	H	<i>α</i> -Naphthyl	<i>cis</i>	6.38 (s)	6.12 (q)	5.8 (d)	6.8-7.8 (m)	
7	H	<i>α</i> -Naphthyl	<i>trans</i>	6.75 (s) 6.68-7.8 (m) + aromatics	6.12 (q) (J _{3,4} = 3.5; J _{4,5} = 1.6)	5.82 (d) (J _{3,4} = 3.5; J _{4,5} = 1.6)		
8	H	<i>β</i> -Naphthyl	<i>cis</i>	unresolved multiplet	6.34-7.9 (m)			
9	H	<i>β</i> -Naphthyl	<i>trans</i>	7.1-7.9 (m) + aromatics	6.39 (s)	6.39 (s)		
10	Methyl	<i>α</i> -Naphthyl	<i>cis</i>	6.29-7.89 (m) + aromatics	6.12 (d) (J _{3,4} = 3.5)	5.7 (d) (J _{3,4} = 3.5)		2.28 (s)
11	Methyl	<i>α</i> -Naphthyl	<i>trans</i>	6.63-7.55 (m) + aromatics	5.7 (s)	5.7 (s)		2.26 (s)

(a) Chemical shift given in ppm (δ). (b) Coupling constants given in Hz. (c) Protons H₃ and H₄ as well as ethylenic protons as a 2H singlet at the same δ value; s = singlet, d = doublet, q = quartet.