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Note

Stereoisomeric 2-Naphthyl-3-furylacrylic Acids. Synthesis, Separation and Identification[a,b]

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Some new 2-(α-naphthyl)- and 2-(β-naphthyl)-3-furylacrylic acids were synthetized by modified Perkin reaction. The separable mixture of stereoisomeric acids were obtained in each case. The identity of *Z* and *E* isomers were assigned on the basis of NMR data.

INTRODUCTION

Diarylethylenes are a very useful system for studing the effects of substituents and geometry of the molecule to their excited states, the photochemical behaviour and mass spectrometry fragmentation pattern. Certain types of such molecules, i. e. heterocyclic analogues of stilbene-like compounds deserve a special attention.

As a part of our continuing interest in the chemistry of furan compounds, the photochemical *cis-trans* isomerizations[1] and photodehydrocyclization[2] of some substituted furylacrylic acids were reported.

This paper describes the preparation of naphthyl-substituted furylacrylic acids, the separation of stereoisomers and their identification requisite for the photochemical studies which are in progress and will be reported elsewhere. The title compounds were synthetized by a modified Perkin condensation[3] starting from α-naphthyl- or β-naphthyl-acetic acid and 2-furfural or 5-methyl-2-furfural (Scheme 1).

Similarly to the reported examples[1,4] it was possible to separate *E* from *Z* isomers of the studied acids I—IV by means of successive acidification of their sodium salts. After the separation of *E* stereoisomer which precipitated first at pH 6, the remaining solution on acidification to pH 1—2 with conc. hydrochloric acid yielded *Z* stereoisomer. The relative contribution of *E* and *Z* isomers varied from 98 : 2 to 84 : 16 in favour of the *E* isomer.

The ratio depends to some extent upon the starting naphthylacetic acid since it was noted that α-naphthylacetic acid yielded a reaction product containing 1—5% of the *Z* isomer, while the product from β-naphthylacetic acid contained 10—15% of *Z* isomer.

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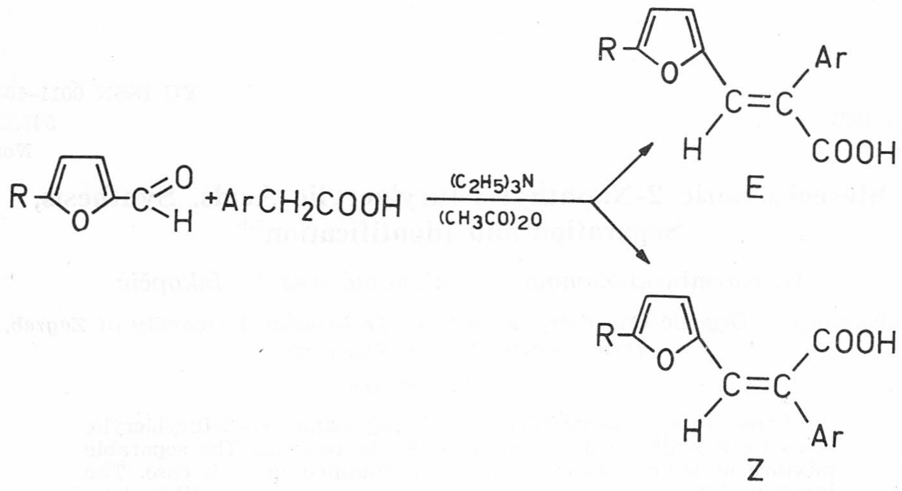
[a] Studies in the Furan Series. XVII; For part XVI see: G. Karminski-Zamola and K. Jakopčić, *Bull. Sci. Conseil Acad. RSF Yougosl.* **21** (1976) 134.

[b] Presented in part at the *Second Yugoslaw Congress of Industrial Chemistry*, Skopje, June 1—4, 1976.



R = H, CH_3; Ar = α-naphthyl, β-napthtyl.

Scheme 1.

The ^1H NMR spectra of the corresponding *E* and *Z* acids exhibit a significant difference in the chemical shift for ethylenic protons (0.9—1.3 ppm) and were of a great assistance and the main criterion in assigning the configuration. The ehylenic protons (H_3) of *E* and *Z* acids were recognized at 7.92—8.00 ppm (δ) and 6.80—6.96 ppm (δ) (Table II), *Z* isomers being shifted to higher field. Signals of the furan ring protons were also affected by configuration but the effect is most pronounced with H_3 protons (Table II). The shift to lower field for *Z* isomer is caused by the anisotropy of the carbonyl group situated close to the H_3 proton. Similar conclusion in case of β-substituted furylacrylates[5] were reported during the preparation of this manuscript.

All prepared compounds (Table I) were characterized by elemental analyses, MS, ir and uv spectra.

EXPERIMENTAL

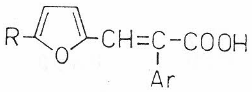
Melting points are uncorrected. The ir spectra were taken on Perkin-Elmer 137 Infracord spectrometer in KBr discs. The uv spectral data were obtained with a Perkin-Elmer 124 spectrophotometer using ethanolic solutions. The ^1H NMR spectra were recorded on a Varian T 60 spectrometer. Chemical shifts are given in ppm (δ) with TMS as internal standard.

General Procedure

A mixture of naphthylacetic acid (0.027 mol) furfural (0.032 mol), triethylamine (4.3 ml) and acetic anhydride (6.7 ml) was heated 1.5—3.5 h at the boiling point. After the reaction was over, the mixture was cooled, acidified with conc. hydrochloric acid and extracted with ether. The organic layer was washed with water and acids reextracted into 5% sodium hydroxide 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 conc. hydrochloric acid was added, and an additional crystalline crop consisting of *Z* isomer was filtered off and recrystallized from benzene/petroleum ether (See Table I).

TABLE I

2-Naphthyl-3-furylacrylic Acids

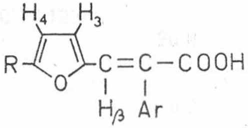


No.	R	Ar	Stereo-isomer	React. time min	Ratio *E* : *Z* %	Yield** %	M. p. °C	Ir/cm^{-1}		Anal. Cal'cd: Found: %	
								C=C	C=O	C	H
I	H*	α-naphthyl	*E*	150	98.2 : 1.8	94.7	207—8	1594	1650	77.25 77.49	4.57 4.62
Ia	H	α-naphthyl	*Z*			1.8	157—9	1594	1673	77.25 77.15	4.57 4.58
II	CH_3	α-naphthyl	*E*	210	94.8 : 5.2	57.5	173—4	1600	1664	77.68 77.43	5.07 4.92
IIa	CH_3	α-naphthyl	*Z*			3.1	142—3	1588	1650	77.68 77.46	5.07 5.12
III	H*	β-naphthyl	*E*	90	84.1 : 15.9	50.2	220—2	1614	1671	77.25 77.39	4.57 4.77
IIIa	H*	β-naphthyl	*Z*			9.5	134—6	1614	1679	77.25 77.02	4.57 4.92
IV	CH_3	β-naphthyl	*E*	90	86.4 : 13.6	50.6	214—5	1607	1671	77.68 77.55	5.07 5.31
IVa	CH_3	β-naphthyl	*Z*			8.0	127—9	1581	1679	77.68 77.35	5.07 5.41

* MS, *m/e* 264 (M^+); ** Yield of pure separated isomer.

TABLE II

^1H *NMR Data for* E *and* Z *Acids*



No.	R	Ar	Konfig.	H_β^a	$H_3^{a,b}$	$H_4^{a,b}$	$H^a_{(CH_3)}$
I	H	α-naphthyl	*E*	8.00(s)	5.43(d) ($J_{3,4} = 3.5$)	6.03(q) ($J_{3,4} = 3.5$; $J_{4,5} = 1.6$)	—
Ia			*Z*	6.80(s)	7.16(d) ($J_{3,4} = 3.0$)	6.60(q) ($J_{3,4} = 3.0$; $J_{4,5} = 1.6$)	—
II	CH_3	α-naphthyl	*E*	7.98(s)	5.38(d) ($J_{3,4} = 3.5$)	5.68(d) ($J_{3,4} = 3.5$)	2.08(s)
IIa			*Z*	6.82(s)	6.04(d) ($J_{3,4} = 3.0$)	5.65(d) ($J_{3,4} = 3.0$)	2.23(s)
III	H	β-naphthyl	*E*	7.92(s)	5.83(d) ($J_{3,4} = 3.8$)	6.13(q) ($J_{3,4} = 3.8$; $J_{4,5} = 1.8$)	—
IIIa			*Z*	6.96(s)	6.76(d) ($J_{3,4} = 3.8$)	6.45(q) ($J_{3,4} = 3.8$; $J_{4,5} = 1.8$)	—
IV	CH_3	β-naphthyl	*E*	7.93(s)	5.76(s)^c	5.76(s)^c	2.10(s)
IVa			*Z*	6.93(s)	6.75(d) ($J_{3,4} = 3.0$)	6.06(d) ($J_{3,4} = 3.0$)	2.33(s)

[a] Chemical shift given in ppm (δ); [b] Coupling constants given in Hz; [c] Protons H_3 and H_4 as a 2H singlet at the same δ value; s = singlet, d = doublet, q = quartet.

TABLE III

Uv Spectral Data from 2-Naphthyl-3-furylacrylic Acids

R	Ar	λ_{max} (log ε)			
		E		*Z*	
H	α-naphthyl	223	(4.81)	222	(4.80)
		283	(4.20)	282	(4.20)
		307	(4.01)	308	(4.31)
CH_3	α-naphthyl	222.5	(4.81)	221.5	(4.76)
		287	(4.14)	283	(4.04)
		325	(4.34)	290	(4.07)
				318	(4.20)
H	β-naphthyl	220	(4.95)	223	(4.92)
		278	(4.25)	257	(3.91)
		288	(4.31)	266	(3.96)
		310	(4.36)	276	(4.05)
				287	(4.05)
				328	(4.17)
CH_3	β-naphthyl	220.5	(4.88)	223	(4.99)
		277	(4.15)	258	(3.97)
		288	(4.22)	267	(4.05)
		314	(4.27)	277	(4.10)
				287	(4.10)
				328	(4.16)

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SAŽETAK

Stereoizomerne 2-naftil-3-furil akrilne kiseline. Sinteza, odvajanje i identifikacija

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U svrhu nastavka naših radova na fotokemijskim reakcijama supstituiranih furilakrilnih kiselina[1,2], priredili smo 2-(α-naftil) i 2-(β-naftil)-3-furilakrilne kiseline definirane konfiguracije modificiranom Perkinovom sintezom. U reakciji je nastala smjesa stereoizomera. Izomeri *Z* i *E* odvojeni su preko njihovih natrijevih soli zakiseljavanjem do različitih pH vrijednosti. Identifikacija stereoizomera izvršena je s pomoću NMR, ir i uv spektroskopije, te elementarnom analizom.

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