

CCA-821

YU ISSN 0011-1643

541.14:547.725

Original Scientific Paper

Photochemical Isomerizations of Furylacrylic Acids^{a)b)}

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Received October 11, 1973

It was shown that *cis*-3-(2'-furyl)acrylic acid (Ib), *cis*-2-methyl-3-(2'-furyl)acrylic acid (IIb), *cis*-3-(5'-methyl-2'-furyl)acrylic acid (IIIb) and *cis*-2-methyl-3-(5'-methyl-2'-furyl)acrylic acid (IVb) can be conveniently prepared by photochemical isomerization of the corresponding *trans* acids (Ia—IVa). The rate of isomerization and the composition of the mixture at photoequilibrium in water-filtered ultraviolet is not influenced by methyl substitution. The isomeric acids were separated through their cyclohexylammonium salts and characterized by elemental analyses, uv. and ir. spectra.

The photochemistry of conjugated arylalkenes has been widely investigated. Stilbene and its derivatives have been a centre of interest for decades and many aspects of their photochemistry are now understood^{1,2}. Simpler conjugated monophenylalkenes have been studied to a limited extent^{3,4}.

More attention has been paid to the photochemistry of cinnamic acids. The irradiation of crystalline *trans*-cinnamic acid with sunlight led mostly to dimeric truxillic and truxinic acids⁵, but to a small extent isomerization to *cis*-cinnamic acid was also observed⁶. On the other hand filtered or unfiltered ultraviolet irradiation of substituted or unsubstituted *trans*-cinnamic acids in solution caused *trans-cis* isomerizations⁷, accompanied in some instances by lactonisation⁸.

As a part of our studies of furans⁹ we turned our attention to photochemical transformations of furylacrylic acids. On irradiation with sunlight or light of a high pressure mercury lamp crystalline 3-(2'-furyl)acrylic acid dimerized to 2-furyl analogue of truxinic acid¹⁰. Similar results were obtained by Lahav and Schmidt¹¹.

To the best of our knowledge there are no reported data about photochemical transformations of unsubstituted or substituted furylacrylic acids in solutions; in the present work we wish to report on photochemically induced *trans-cis* isomerizations of such acids.

Much has been done to increase the understanding of the mechanisms of direct or sensitized *cis-trans* photoisomerizations of olefinic compounds, and to identify the states involved². By direct excitation an electron is

^{a)} Studies in the Furan Series. XIV.

^{b)} Taken in part from the Ph.D. Thesis of G. Karminski-Zamola, University of Zagreb, 1972.

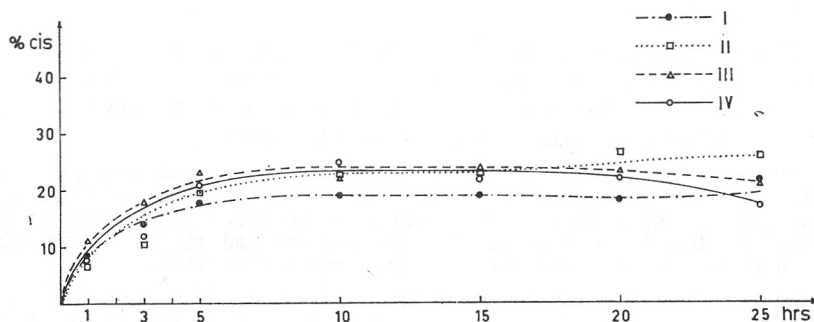


Fig. 1. Relative contribution of *cis* acids (as Me-esters) in photochemical mixture. 10% solutions in glacial acetic acid, water cooled ORIGINAL HANAU TQ-150 high pressure mercury lamp.

It should be noted that uv. maxima of *cis* and corresponding *trans* acids are very near each other, but *cis* acids possess lower absorption intensities (Table I).

TABLE I

Acid	<i>trans</i>		<i>cis</i>	
	$\frac{\lambda_{\max}}{\text{nm}}$	$\log \epsilon$	$\frac{\lambda_{\max}}{\text{nm}}$	$\log \epsilon$
I	296	4.37	299	4.14
II	292	4.41	294	4.15
III	308	4.48	310	4.21
IV	305	4.43	302	4.15

EXPERIMENTAL

Melting points and boiling points are uncorrected. Ir. spectra were taken on a Perkin-Elmer 137 Infracord spectrophotometer using mull technique. Uv. spectra were recorded on Perkin-Elmer 124 spectrophotometer. Ultraviolet irradiations were performed using a water-cooled immersion ORIGINAL HANAU TQ-150 quartz high pressure mercury arc lamp. GLC were performed on an Aerograph 660 chromatograph fitted with a flame ionization detector and a $1/8'' \times 5'$ steel column packed with 3% SE-30 on Aeropak 30 or 3% Carbowax 20 M on Chromosorb T.

trans Acids used in this work, except IVa, were reported and were prepared by known procedures¹⁶⁻¹⁸.

trans-2-Methyl-3-(5'-methyl-2'-furyl)acrylic acid (IVa)

A mixture of 50.0 g (0.46 mol) freshly distilled 5-methylfurfural, 65.0 g (0.46 mol) propionic anhydride and 65.0 g anhydrous potassium propionate was heated 20 h at 160 °C. The reaction mixture was poured into 100 ml water and neutralized with saturated solution of sodium carbonate. Crystalline *trans* acid melting at 115–121 °C was obtained on acidification of the decolorized solution with hydrochloric acid, and was recrystallized from aqueous methanol. Yield 22.0 g, m. p. 130–131 °C.

Anal. $\text{C}_9\text{H}_{10}\text{O}_3$ (166.2) calc'd.: C 65.03; H 6.06%
found: C 65.04; H 6.25%

Ir. spectrum: ν_{\max} 1670 cm^{-1} (C=O) and 1630 cm^{-1} (C=C).

Irradiation experiments

A 10% solution of *trans* acid (Ia—IVa) in glacial acetic acid was irradiated at 20—25 °C until there was no change in melting points of evaporated small aliquots (about 20 h). The dark residue after removal of the solvent, containing *trans* and *cis* acid was treated according to stated procedure.

Procedure A. — A photochemical mixture of *cis* and *trans* acid was triturated with benzene. The less soluble *trans* acid was filtered off. The additional quantity of *trans* acid was separated after the addition of petroleum ether, and the solution evaporated to dryness. The crude *cis* acid was purified by trituration with hot petroleum ether and recrystallization of the evaporation product.

Procedure B. — A photochemical mixture of *cis* and *trans* acid was triturated with hot petroleum ether. The solution was evaporated. After fractional crystallization from petroleum ether crude *cis* acid was obtained. To the hot ethylacetate solution of the acid an equimolar quantity of cyclohexylamine was added. The cyclohexylammonium salt of *trans* acid which crystallized on cooling was filtered off and the filtrate evaporated. To the residue a 5% aqueous potassium hydroxide was added, and the solution extracted with ether. Pure, crystalline *cis* acid was obtained on acidification with 5% sulfuric acid.

cis-3-(2'-Furyl)acrylic acid (Ib)

From 7.0 g *trans*-3-(2'-furyl)acrylic acid¹⁶ (m.p. 139—140 °C). The mixture of *cis* and *trans* acid was elaborated according to Liebermann's procedure^{13,14}. The crystalline Ib (1.0 g) melting at 106—108 °C was obtained*.

cis-2-Methyl-3-(2'-furyl)acrylic acid (IIb)

From 20.0 g *trans*-2-methyl-3-(2'-furyl)acrylic acid¹⁷ (m.p. 118—119 °C). Procedure B. Yield 2.0 g, m.p. 72—73 °C.

Anal. C₉H₈O₃ (152.1) calc'd.: C 63.15; H 5.32%
found: C 63.26; H 5.59%

Ir. spectrum: ν_{\max} 1670 cm⁻¹ (C=O) and 1600 cm⁻¹ (C=C).

cis-3-(5'-Methyl-2'-furyl)acrylic acid (IIIb)

By irradiation of 4.5 g *trans*-3-(5'-methyl-2'-furyl)acrylic acid¹⁸ (m.p. 156—157 °C). Procedure A. Yield 0.6 g, m.p. 110—112 °C.

Anal. C₉H₈O₃ (152.1) calc'd.: C 63.15; H 5.32%
found: C 63.38; H 5.02%

Ir. spectrum: ν_{\max} 1680 cm⁻¹ (C=O) and 1625 cm⁻¹ (C=C).

cis-2-Methyl-3-(5'-methyl-2'-furyl)acrylic acid (IVb)

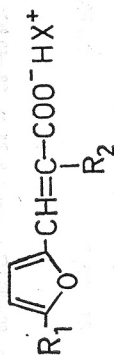
From 20.0 g *trans*-acid IVa (m.p. 130—131 °C). Procedure B. Yield 2.9 g, m.p. 80—82 °C.

Anal. C₉H₁₀O₃ (166.2) calc'd.: C 65.03; H 6.06%
found: C 64.90; H 6.21%

Ir. spectrum: ν_{\max} 1680 cm⁻¹ (C=O) and 1600 cm⁻¹ (C=C).

*Liebermann¹³ stated m.p. 104—105 °C for the sample of *cis* acid Ib prepared besides *trans* isomer Ia by decarboxylation of furfurylidenemalononic acid and separation of both isomers.

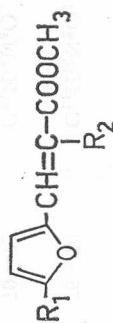
TABLE II
Phenylhydrazonium and Cyclohexylammonium Salts



R ₁	R ₂	isomer	X	M. p. °C	Formula	Mol. weight	Anal.			calcd found	
							% C	% H	% N	% C	% H
H	H	<i>trans</i>	C ₆ H ₈ N ₂ ^a	88—90	C ₁₃ H ₁₄ N ₂ O ₃	246.2	63.40 63.18	5.73 5.53		11.38 11.28	
H	H	<i>cis</i>	C ₆ H ₈ N ₂	83—84	C ₁₃ H ₁₄ N ₂ O ₃	246.2	63.40 63.19	5.73 5.85			
H	CH ₃	<i>trans</i>	C ₆ H ₈ N ₂	79—80	C ₁₄ H ₁₆ N ₂ O ₃	260.3	64.60 64.86	6.20 6.49			
H	CH ₃	<i>trans</i>	C ₆ H ₁₃ N ^b	171—172	C ₁₄ H ₂₁ NO ₃	251.3	66.90 67.21	8.42 8.10		5.57 5.42	
H	CH ₃	<i>cis</i>	C ₆ H ₁₃ N	150—151	C ₁₄ H ₂₁ NO ₃	251.3	66.90 66.95	8.42 8.21			
CH ₃	H	<i>trans</i>	C ₆ H ₈ N ₂	67—68	C ₁₄ H ₁₆ N ₂ O ₃	260.3	64.60 64.57	6.20 5.92			
CH ₃	H	<i>cis</i>	C ₆ H ₈ N ₂	76—78	C ₁₄ H ₁₆ N ₂ O ₃	260.3	64.60 64.23	6.20 5.92			
CH ₃	CH ₃	<i>trans</i>	C ₆ H ₈ N ₂	70—72	C ₁₅ H ₁₈ N ₂ O ₃	274.3	65.67 65.43	6.61 6.82			
CH ₃	CH ₃	<i>trans</i>	C ₆ H ₁₃ N	153—154	C ₁₅ H ₂₃ NO ₃	265.3	67.89 68.05	8.74 8.50		5.28 5.48	

^a Phenylhydrazine ^b Cyclohexylamine

TABLE III
Methyl esters of cis- and trans-furylacrylic acids



R ₁	R ₂	isomer	yield %	B. p. °C/mmHg	Formula	Mol. weight.	Anal.		calcd found
							% C	% H	
H	H	<i>trans</i>	57	92—95/6 ^{a,b}	C ₈ H ₈ O ₃	152.1			
H	H	<i>cis</i>	33	75—76/5	C ₈ H ₈ O ₃	152.1	63.15 62.96		5.32 5.50
H	CH ₃	<i>trans</i>	36	99—101/5 ^c	C ₉ H ₁₀ O ₃	166.2			
H	CH ₃	<i>cis</i>	58	70—71/10	C ₉ H ₁₀ O ₃	166.2	65.03 65.00		6.06 6.30
CH ₃	H	<i>trans</i>	55	89—90/5 ^{d,e}	C ₉ H ₁₀ O ₃	166.2			
CH ₃	H	<i>cis</i>	55	72—73/5	C ₉ H ₁₀ O ₃	166.2	65.03 64.68		6.06 6.36
CH ₃	CH ₃	<i>trans</i>	35	68—69/5	C ₁₀ H ₁₂ O ₃	180.2	66.65 66.35		6.71 6.70
CH ₃	CH ₃	<i>cis</i>	92	81—85/5	C ₁₀ H ₁₂ O ₃	180.2	66.65 66.39		6.71 6.59

^a m. p. 29 °C; ^b Lit.²⁰ b. p. 95—97 °C/6 mmHg; ^c Lit.²¹ b. p. 89—90 °C/5 mmHg; ^d M. p. 39—40 °C; ^e Lit.¹⁶ b. p. 88—90 °C/5 mmHg; ^f M. p. 27 °C.

The preparation of salts (Table II)

Phenylhydrazonium salts. — To the saturated ether solution of a particular acid an equimolar quantity of phenylhydrazine was added. The salt soon crystallized, and was usually of analytical purity. It should be noted that the salts of *cis* acid with methyl substituent in position 2 (IIb and IVb) could not be obtained.

Cyclohexylammonium salts. — To the solution of the acid in a minimum amount of ethylacetate an equimolar quantity of cyclohexylamine was added. A quantitative yield of crystalline salt was separated and recrystallized from benzene. Crystalline cyclohexylammonium salt of IVb could not be obtained.

The preparation of methyl esters (Table III)

To the ethereal solution of the acid an excess of diazomethane* was added. After evaporation *in vacuo* methyl ester was distilled twice at reduced pressure.

Infrared absorption of esters at 1725—1690 cm^{-1} and 1650—1620 cm^{-1} (C=O and C=C).

Acknowledgement. This work has been financially supported by Research Fund of Croatia. We are indebted to late Prof. V. Hahn for suggesting the problem and for stimulating discussion in the early stage of the work. The authors wish to thank Mrs. I. Guštak-Mašek for the microanalyses.

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* The diazomethane solution was prepared according to DeBoer and Backer¹⁹.

SAŽETAK**Fotokemijska izomerizacija furilakrilnih kiselina***G. Karminski-Zamola i K. Jakopčić*

Ultraljubičastim osvjetljavanjem lako pristupačnih *trans*-izomera (Ia—IVa) u ledenoj octenoj kiselini s pomoću vodom hlađena ORIGINAL HANAU TQ-150 živina luka visokog tlaka i naknadnom separacijom izomera dobivene su *cis*-3-(2'-furil)akrilna (Ib), *cis*-2-metil-3-(2'-furil)akrilna (IIb), *cis*-3-(5'-metil-2'-furil)akrilna (IIIb) i *cis*-2-metil-3-(5'-metil-2'-furil)akrilna kiselina (IVb). Pokazalo se da brzina fotokemijske izomerizacije kao i sastav smjese u fotoravnoteži pod primijenjenim uvjetima ne ovise o metil-supstituciji. Izomerne kiseline karakterizirane su elementarnom analizom, ir. i uv. spektrima, te kao metilni esteri, cikloheksilamonijeve ili fenilhidrazonijeve soli.

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Primljeno 11. listopada 1973.