Photochemical Isomerizations of Furyleacrylic Acids

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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 understood1,2. Simpler conjugated monophenylalkenes have been studied to a limited extent3,4. 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 furyleacrylic 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 furyleacrylic 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.
promoted from the highest filled bonding $\pi$ orbital to the lowest antibonding $\pi^*$ orbital. It can be shown that the most stable geometric configuration of both the singlet and triplet ($\pi$, $\pi^*$) states of ethylene and its derivatives are highly twisted from the planar ground state about the double bond axis. In this form, the distinction between cis and trans is lost and the excited molecule can easily return to either cis or trans olefin ground state, though not with equal probability\textsuperscript{12}. Since the isomer of lower ground state stability is frequently formed in higher yield, the process is useful synthetically.

The various syntheses of unsubstituted or alkyl substituted furylacrylic acids usually give the more stable trans isomer. A successful photochemical isomerization of generally easy obtainable trans-furylacrylic acids to their cis isomers followed by appropriate separation seems to be a very useful method for preparing cis acids of this type, since the only reported example of cis-acid was cis-3-(2'-furyl)acrylic acid prepared besides trans isomer by Liebermann\textsuperscript{13,14}.

Another reason for undertaking this research was to study the influence of methyl substitution on photochemical isomerization of trans-furylacrylic acids in solution:

\[
\begin{align*}
\text{R}_1 & \quad \text{C} \quad \text{C} \quad \text{COOH} \\
\text{H} & \quad \text{H} \\
\text{I} & \quad \text{R}_1=\text{H} \quad \text{R}_2=\text{H} \\
\text{II} & \quad \text{R}_1=\text{H} \quad \text{R}_2=\text{CH}_3 \\
\text{III} & \quad \text{R}_1=\text{CH}_3 \quad \text{R}_2=\text{H} \\
\text{IV} & \quad \text{R}_1=\text{CH}_3 \quad \text{R}_2=\text{CH}_3
\end{align*}
\]

Sandris\textsuperscript{15} found that methyl substitution either in position 2 or 3 of trans-cinnamic acid had no influence on the rate of photochemical isomerization induced by uv.-irradiation of $4 \times 10^{-4}$ M solutions, but the percentage of cis isomer in the photostationary state was influenced by such substitution.

In our investigations on furylacrylic acids, neither the rate of isomerization nor the percentage of cis and trans isomer was influenced by methyl substitution. The photostationary state under our experimental conditions was established at about 20% cis isomer after a 5 h of water-filtered ultraviolet irradiation of 10% solutions in glacial acetic acid.

The rate of photochemically induced isomerization and the composition of the photoequilibrium mixture was determined by GLC-analyses of esterified aliquots taken during irradiation of the particular furylacrylic acid (Fig. 2.).

cis-Furylacrylic acids were separated from the photochemical mixture on the basis of different solubilities of the isomeric acids in benzene or petroleum ether. Final purification was performed by fractional crystallizations of corresponding piperidine or cyclohexylamine salts followed by regeneration of acids.

The acids, their salts and methyl esters were characterized by elemental analyses, uv. and ir. spectra.
ISOMERIZATIONS OF FURYLACRYLIC ACIDS

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>
<thead>
<tr>
<th>Acid</th>
<th>trans $\lambda_{max}$ nm</th>
<th>log $\varepsilon$</th>
<th>cis $\lambda_{max}$ nm</th>
<th>log $\varepsilon$</th>
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<tbody>
<tr>
<td>I</td>
<td>296</td>
<td>4.37</td>
<td>299</td>
<td>4.14</td>
</tr>
<tr>
<td>II</td>
<td>292</td>
<td>4.41</td>
<td>294</td>
<td>4.15</td>
</tr>
<tr>
<td>III</td>
<td>308</td>
<td>4.48</td>
<td>310</td>
<td>4.21</td>
</tr>
<tr>
<td>IV</td>
<td>305</td>
<td>4.43</td>
<td>302</td>
<td>4.15</td>
</tr>
</tbody>
</table>

EXPERIMENTAL

Melting points and boiling points are uncorrected. Ir. spectra were taken on a Perkin-Elmer 137 Infraord 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 chromato-graph fitted with a flame ionization detector and a 1/8" x 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 decolourized solution with hydrochloric acid, and was recrystallized from aqueous methanol. Yield 22.0 g, m. p. 130—131 °C.

Anal. C$_9$H$_{10}$O$_3$ (166.2) calcd.: C 65.03; H 6.06% found: C 65.04; H 6.25%

Ir. spectrum: $\nu_{max}$ 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 hydroxyde 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 procedure13, 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. C₈H₈O₃ (152.1) calc’d.: C 63.15; H 5.32%
found: C 63.26; H 5.59%

Ir. spectrum: \(v_{\text{max}}\) 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. C₈H₈O₃ (152.1) calc’d.: C 63.15; H 5.32%
found: C 63.38; H 5.02%

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

*Liebermann19 stated m. p. 104—105 °C for the sample of cis acid Ib prepared besides trans isomer Ia by decarboxylation of furfurylidemalonic acid and separation of both isomers.
### Phenylhydrazine and Cyclohexylammonium Salts

**Table II**

<table>
<thead>
<tr>
<th>R&lt;sub&gt;1&lt;/sub&gt;</th>
<th>R&lt;sub&gt;2&lt;/sub&gt;</th>
<th>Isomer</th>
<th>M. p. °C</th>
<th>Mol. formula</th>
<th>Mol. weight</th>
<th>Calc'd % C</th>
<th>Found % C</th>
<th>Calc'd % H</th>
<th>Found % H</th>
<th>Calc'd % N</th>
<th>Found % N</th>
</tr>
</thead>
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<tr>
<td>H</td>
<td>H</td>
<td>trans</td>
<td>88-90</td>
<td>C₁₃H₁₅N₂O₂⁻</td>
<td>246.2</td>
<td>63.40</td>
<td>63.18</td>
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<td>5.33</td>
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<td>6.39</td>
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<td>cis</td>
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<td>C₁₃H₁₃N₂O₂⁻</td>
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<td>63.40</td>
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<td>H</td>
<td>trans</td>
<td>79-80</td>
<td>C₁₄H₁₉N₂O₃⁻</td>
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<td>64.60</td>
<td>64.86</td>
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<td>C₁₄H₂₁N₂O₃⁻</td>
<td>280.3</td>
<td>64.60</td>
<td>64.86</td>
<td>6.20</td>
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<td>280.3</td>
<td>64.60</td>
<td>64.86</td>
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<td>5.77</td>
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<td>cis</td>
<td>79-80</td>
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<td>65.67</td>
<td>65.43</td>
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<td>6.82</td>
<td>6.61</td>
<td>5.85</td>
<td>5.64</td>
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</table>

**Note:** Analyzed and calculated data may vary. The observed molar weight and composition are reported for each compound.
### TABLE III

*Methyl esters of cis- and trans-furylacrylic acids*

![Structural formula](image)

<table>
<thead>
<tr>
<th>R₁</th>
<th>R₂</th>
<th>isomer</th>
<th>yield %</th>
<th>B.p. °C/mmHg</th>
<th>Formula</th>
<th>Mol. weight</th>
<th>Anal.</th>
<th>calc’d found</th>
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<tbody>
<tr>
<td>H</td>
<td>H</td>
<td>trans</td>
<td>57</td>
<td>92—95/6&lt;sup&gt;a,b&lt;/sup&gt;</td>
<td>C₅H₅O₃</td>
<td>152.1</td>
<td>63.15</td>
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<tr>
<td>H</td>
<td>H</td>
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<td>33</td>
<td>75—76/5</td>
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<td>152.1</td>
<td>65.03</td>
<td>65.00</td>
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<tr>
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<td>CH₃</td>
<td>trans</td>
<td>36</td>
<td>99—101/5&lt;sup&gt;3&lt;/sup&gt;</td>
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<td>166.2</td>
<td>66.65</td>
<td>66.35</td>
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<td>55</td>
<td>89—90/5&lt;sup&gt;d,e&lt;/sup&gt;</td>
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<td>166.2</td>
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<td>180.2</td>
<td>66.65</td>
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</tbody>
</table>

<sup>a</sup> m. p. 29 °C;  <sup>b</sup> Lit.<sup>28</sup> b. p. 95—97 °C/6 mmHg;  <sup>c</sup> Lit.<sup>21</sup> b. p. 89—90 °C/5 mmHg;  <sup>d</sup> M. p. 39—40 °C;  <sup>e</sup> Lit.<sup>14</sup> b. p. 88—90 °C/5 mmHg;  <sup>f</sup> 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).

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**REFERENCES**

1. See e. g.
   b) J. Saltiel, ibid. 50 (1968) 6394.


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* The diazomethane solution was prepared according to DeBoer and Backer.\(^{19}\)
SAŽETAK
Fotokemijska izomerizacija furilakrilnih kiselina

G. Karminski-Zamola i K. Jakopčić

Ultraljubičastim osvjetljavaњem lako pristupačnih trans-izomera (Ia—IVA) u ledenoj octenoj kiseline 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 fotoravnotezi pod primijenjenim uvjetima ne ovise o metil-supstituciji. Izomerna kiseline karakterizirane su elementarnom analizom, ir. i uv. spektrom, te kao metilni esteri, cikloheksilamonijeve ili fenilhidrazonijeve soli.

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