

## PREPARATION OF GEOMETRIC ISOMERS OF 2-(2-BROMOVINYL)-5-NITROFURAN\*

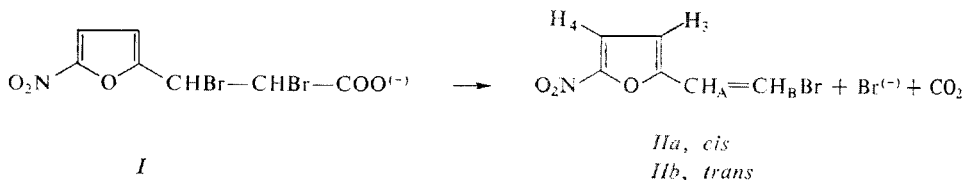
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Elimination reactions of the addition product of bromine to *trans*-3-(5-nitro-2-furyl)acrylic acid [*erythro*-2,3-dibromo-3-(5-nitro-2-furyl)propionic acid (*I*)] have been studied in water and in acetone as the preparative route to 2-(2-bromovinyl)-5-nitrofuran.

Aiming at the synthesis of new nitrofuran derivatives we investigated the preparation of the hitherto not prepared 2-(2-bromovinyl)-5-nitrofuran (*Ia, b*) which is formed in the debrominative decarboxylation of sodium salt of 2,3-dibromo-3-(5-nitro-2-furyl)propionic acid (*I*) according to the following Scheme:



It is known that anions of  $\beta$ -halo acids are decomposed on heating with weak bases under formation of olefin, carbon dioxide and halide anion<sup>1-6</sup>. The mechanism of the decomposition of  $\beta$ -aryl- $\beta$ -halo acids anions was studied by several authors<sup>1,3,5,6</sup>. Only one case of this reaction involving a furan derivative was hitherto reported by Gibson and Kahnweiler<sup>7,8</sup> who decomposed bromination product of furylacrylic acid in water.

We carried out the elimination reactions either in acetone, in which almost no effects of substituents attached to the furan nucleus were observed, or in water which is a very suitable solvent for anions and in which substituents on the furan nucleus strongly influence the course and products of the reaction. The addition of bromine to *trans*-3-(5-nitro-2-furyl)acrylic acid afforded *erythro*-2,3-dibromo-3-(5-nitro-2-furyl)propionic acid (*I*). Its *erythro* configuration was determined by the reaction with

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an alcoholic solution of potassium iodide which regenerated *trans*-3-(5-nitro-2-furyl)acrylic acid<sup>9,10</sup>. The acid *I* afforded a product (80%) which did not contain any carboxyl group and which upon crystallisation gave the pure *cis*-isomer *Ila* in 76% yield.

The compound *Ila* is thermally stable. Under the conditions of decarboxylative elimination the starting *cis*-isomer *Ila*, m.p. 37–40°C, was regenerated. The compound is isomerised to its *trans*-derivative (*Ilb*) on irradiation with UV light. When exposed to daylight, the sample slowly turns brown.

According to the results obtained, the decomposition of the anion of the acid *I* in acetone is most probably a stereospecific *trans*-elimination<sup>2,4</sup>. The acid anion is decomposed by a mechanism, analogous to the E2 elimination of alkyl halides. Cristol and Norris<sup>2</sup> named this reaction type debrominative decarboxylation.

Elimination in an aqueous solution afforded, according to gas-liquid chromatographic analysis, 28% of *trans*-2-(2-bromovinyl)-5-nitrofuran (*Ilb*) and 72% of its *cis*-isomer *Ila*. The structure of the product was confirmed by <sup>1</sup>H-NMR spectroscopy and mass spectrometry. In aqueous solution the reaction proceeds most probably by a monomolecular mechanism discussed in ref.<sup>2</sup>. The strong influence of the nitro group in the position 5 of the furan nucleus prefers one conformer and suppresses the E1 course as evidenced by the relative ratio of stereoisomers *Ilb* : *Ila* (28 : 72). These results are in accord with that obtained for a dibrominative decarboxylation<sup>5</sup> where pure *cis*-isomer is formed in ethanol whereas in water a mixture of stereoisomers was isolated (*trans* : *cis* = 33 : 67).

The isomers *Ila* and *Ilb* were assigned the configuration on the basis of their <sup>1</sup>H-NMR spectra. Table I shows the marked differences in the coupling constants between the vinyl protons in the isomers.

## EXPERIMENTAL

Melting points were determined on a Kofler block and are uncorrected. The <sup>1</sup>H-NMR spectra were taken on a Tesla NMR BS 487C 80 MHz instrument with tetramethylsilane as the internal standard. Gas-liquid chromatographic analyses were carried out on a Hewlett-Packard 7620A chromatograph with two columns (2 · 10<sup>-3</sup> m – 1.6 m) filled with 10% OV-17 on Chromosorb W; flame ionisation detector. The temperature was programmed from 120°C to 200°C, temperature rise 4°C min<sup>-1</sup>, carrier gas N<sub>2</sub>, flow rate 35 ml min<sup>-1</sup>. The relative ratio of *E* and *Z* isomers, determined under assumption of identical detector response, was found to be 0.3296 using a Hewlett-Packard 10A integrator-calculator. The retention times of *Ilb* and *Ila* were 10.23 min and 10.55 min, respectively. The mass spectra were measured on a MS 902 S (AEI) spectrometer.

### *erythro*-2,3-Dibromo-3-(5-nitro-2-furyl)propionic Acid (*I*)

Addition of bromine to *trans*-3-(5-nitro-2-furyl)acrylic acid (m.p. 234°C) in glacial acetic acid<sup>11</sup> afforded in 71% yield the compound *I*, m.p. 146–7°C (benzene); reported<sup>11</sup> m.p. 142–146°C.

TABLE I  
<sup>1</sup>H-NMR Spectral Data for Compounds II

Isomer		$\delta$ (p.p.m.) <sup>a</sup>	$J_{AB}$ (Hz)	Isomer		$\delta$ (p.p.m.) <sup>a</sup>	$J_{AB}$ (Hz)
<i>Ila</i>	H <sub>A</sub>	7.12 (d, 1 H)	8.5	<i>Ilb</i>	H <sub>A</sub>	7.25 (d, 1 H)	14.5
	H <sub>B</sub>	6.78 (d, 1 H)			H <sub>B</sub>	6.92 (d, 1 H)	
	H <sub>3</sub>	7.29 (d, 1 H)	4.0				
	H <sub>4</sub>	7.39 (d, 1 H)					

<sup>a</sup> Taken in CDCl<sub>3</sub>, tetramethylsilane.

*cis*-2-(2-Bromovinyl)-5-nitrofurán (*Ila*)

*a*) A mixture of *I* (27 g; 0.08 mol) and sodium carbonate (20 g) in acetone (500 ml) was refluxed for 10 hours. The solvent was distilled off, the residue was treated with water (300 ml) and the organic compound was taken into ether. The ether extracts were washed with water, dried over MgSO<sub>4</sub> and taken down, affording the crude *Ila* (14 g; 80%). Recrystallisation from methanol gave needles (13 g), m.p. 38–39.5°C (vesicant!) which were purified by steam distillation. For C<sub>6</sub>H<sub>4</sub>BrNO<sub>3</sub> (218.0) calculated: 6.42% N, 36.65% Br; found: 6.50% N, 36.85% Br. Mass spectrum *m/e*: 217–219 (C<sub>6</sub>H<sub>4</sub>BrNO<sub>3</sub>, 100% M<sup>+</sup>), 187–189 (C<sub>6</sub>H<sub>4</sub>BrO<sub>2</sub>, 50% M–NO), 143–145 (C<sub>5</sub>H<sub>4</sub>Br, 39% M–NO<sub>2</sub>–CO), 105–107 (C<sub>2</sub>H<sub>2</sub>Br, 10%). For <sup>1</sup>H-NMR spectrum see Table I. UV spectrum (methanol): 240 nm (log  $\epsilon$  = 3.93), 260 nm (log  $\epsilon$  = 3.77), 345 nm (log  $\epsilon$  = 4.18).

*b*) A solution of *I* (8.1 g; 0.024 mol) and Na<sub>2</sub>CO<sub>3</sub> (2 g) in water (300 ml) was refluxed for 6 hours, cooled and extracted four times with ether (200 ml). The combined ethereal extracts were washed with water, dried over MgSO<sub>4</sub> and taken down leaving 2 g (40%) of an oil, containing 28% *Ilb* and 72% *Ila*, according to gas-liquid chromatography. The oil deposited 1.24 g of crystals, m.p. 37–40°C, which were shown by <sup>1</sup>H-NMR spectra and gas-liquid chromatography to be the isomer *Ila*.

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