

PREPARATION AND ELECTRON TRANSFER-INDUCED *cis-trans*
ISOMERIZATION REACTIONS OF 1-(5-NITRO-2-FURYL)-, 1-(5-NITRO-2-
-THIENYL)-, AND 1-(4-NITROPHENYL)-2-R ETHYLENES

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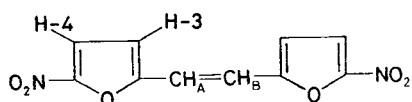
Mixtures of *E*- and *Z*-isomers of 1,2-bis(5-nitro-2-furyl)ethylene (*I*), 1-(5-nitro-2-furyl)-2-(4-nitrophenyl)ethylene (*II*), 1,2-bis(4-nitrophenyl)ethylene (*III*), 1-(5-methoxycarbonyl-2-furyl)-2-(4-nitrophenyl)ethylene (*IV*), 1-(5-methoxycarbonyl-2-furyl)-2-(5-nitro-2-furyl)ethylene (*V*) and 1-(5-methoxycarbonyl-2-furyl)-2-(5-nitro-2-thienyl)ethylene (*VI*) were prepared by the Wittig reaction. These derivatives were isomerized by electron transfer-induced reactions via the radical anion in the CT-complex using aniline as electron donor at 25°C in the light or at 80°C in the dark. The starting as well as the final *E* : *Z* ratio was determined by ¹H NMR spectroscopy. In all cases only the *cis* → *trans* isomerization was observed.

One-electron reductions play an important role both in chemistry^{1,2} and in biology^{3,4}. Depending on the character of the substrate, the arising radical anion may undergo various changes or may be oxidized back to the neutral molecule by a component with higher electron affinity. When the molecule is capable of cleaving X⁻ from the radical anion RX^{-•}, in most cases this reaction takes place (followed by consecutive reactions)^{5,6}. This behaviour was also observed in biological systems, (see e.g., ref.⁷). Another situation exists with molecules that contain a double bond and may thus, in principle, undergo isomerization in the state of the radical anion. The *cis* ⇌ *trans* isomerization is of considerable significance in chemistry⁸⁻¹⁰ as well as biology².

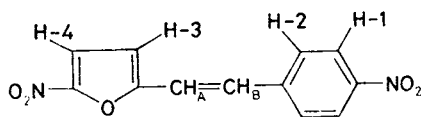
The importance of *cis-trans* isomerases for the intermediary metabolism in animals and bacteria is known. Since enzymes may act as electron donors, some of these isomerizations, induced by electron transfer from the enzyme to the substrate, were studied. Compounds reacting in this way also include nitro derivatives which form radical anions in the first step of metabolic degradation^{11,12}. Interestingly, not all nitro compounds behave in this manner¹³. The group of aromatic nitro derivatives encompasses also 5-nitrofurans which are relatively often used in human and veterinary medicine. In the case of 5-nitro-2-furylethylene derivatives, which are obtained already as mixtures of *cis*- and *trans*-isomers, the electron transfer-induced *cis-trans* isomerization was indeed observed. Tatsumi and co-workers¹⁴ described

cis-trans isomerization in 3-(5-nitro-2-furyl)-2-(2-furyl)acrylamide and 3-(5-nitro-2-furyl)-2-(5-bromo-2-furyl)acrylamide with the enzyme xanthine oxidase as electron donor. The same authors¹⁵ also investigated the isomerization of 3-(5-nitro-2-furyl)-2-phenyl-acrylamide and 3-(5-nitro-2-furyl)-2-(2-furyl)acrylonitrile, induced by several enzymes. In the mentioned cases both the *cis* → *trans* and *trans* → *cis* isomerizations were observed.

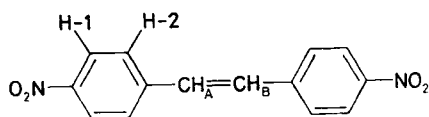
To verify the above-mentioned isomerization reactions in the chemical way, we modelled these processes chemically¹⁶. In the present work we synthesized by Wittig reaction the following electron acceptors: 1,2-bis(5-nitro-2-furyl)ethylene (*I*), 1-(5-nitro-2-furyl)-2-(4-nitrophenyl)ethylene (*II*), 1,2-bis(4-nitrophenyl)ethylene (*III*), 1-(5-methoxycarbonyl-2-furyl)-2-(4-nitrophenyl)ethylene (*IV*), 1-(5-methoxycarbonyl-2-furyl)-2-(5-nitro-2-furyl)ethylene (*V*) and 1-(5-methoxycarbonyl-2-furyl)-2-(5-nitro-2-thienyl)ethylene (*VI*).



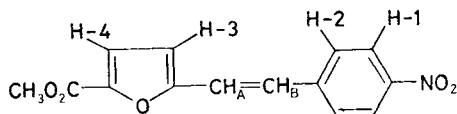
Ia (E)
Ib (Z)



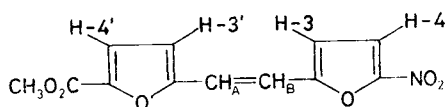
IIa (E)
IIb (Z)



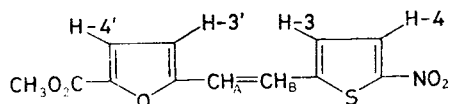
IIIa (E)
IIIb (Z)



IVa (E)
IVb (Z)



Va (E)
Vb (Z)



VIa (E)
VIb (Z)

We have found that the ratio of *E*- and *Z*-isomers, prepared by the Wittig reaction, depends on the experimental technique. Thus, for example, the ethylene derivative *III* was obtained as an 11 : 89 mixture of *E*- and *Z*-isomers when sodium methoxide was added to a mixture of bromide *XI* and 4-nitrobenzaldehyde, whereas when 4-nitrobenzaldehyde was added to the ylide, the *E* : *Z* ratio was 33 : 67. This behaviour was observed also in other cases (see Experimental). For derivative *II*, the *E* : *Z* ratio varied according to whether the reaction started from the bromide *VIII* and 4-nitro-

benzaldehyde or the phosphonium bromide *XI* and 5-nitro-2-furaldehyde. The yields also depended on the experimental procedure: in minimum amounts of methanol the reaction mixture deposited the product in high yield and sufficient purity.

Aniline or *N,N*-diethylaniline were used as electron donors and the isomerization reactions were carried out at 25°C in the presence of light or at 80°C in the dark. The *E* : *Z* ratio before and after the isomerization was determined by ¹H NMR spectroscopy. Since the isomer ratio changed during chromatography, the pure geometric isomers were obtained by fractional crystallization from chloroform-hexane

TABLE I
cis-trans Isomerizations in aniline at 80°C in the dark (25 h)

Compound	<i>E</i> : <i>Z</i>		Conversion, %
	before isomerization	after isomerization	
<i>II</i>	64/36	100/0	100
<i>III</i>	11/89	15/85	5.4
<i>IV</i>	75/25	87/13	47
<i>V</i>	71/29	100/0	100
<i>VI</i>	65/35	94/6	82

TABLE II
UV spectra (λ_{\max} , nm) of ethylene derivatives *I*–*VI* in methanol and of their CT-complexes in aniline and *N,N*-diethylaniline at 25°C

Compound	Solvent		
	methanol	aniline	<i>N,N</i> -diethylaniline
<i>I</i>	412 (427i)	438	486
<i>II</i>	384 (373i)	400	432
<i>III</i>	339	362	417
<i>IV</i>	376 (393i)	393	— ^a
<i>V</i>	408 (425i)	437	— ^a
<i>VI</i>	418 (438i)	450	— ^a

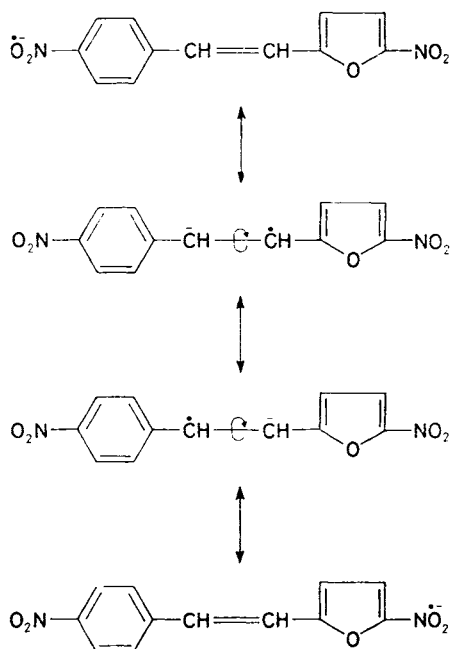
^a Not determined.

(1 : 1) mixture. The isomerizations were performed only with mixtures of *E*- and *Z*-isomers; the ^1H NMR spectral assignment was done with the pure isomers.

Our isomerization experiments were based on the experimentally proven facts that the *cis*-*trans* isomerizations proceed via a CT-complex^{8,9,17-19} and further on theoretical considerations concerning the physical properties of CT-complexes of strong electron acceptors (A) and strong electron donors (D) (Eq. (1)).



In the stage of the tight ion pair, formed by the radical anion and radical cation, the former may isomerize. This stage is influenced by many factors which have been analyzed in the SET (Single Electron Transfer) processes as well as at other occasions²⁰⁻²⁶. Nevertheless, the fact is that, in principle, these isomerization reactions may proceed even in the dark²⁷. Some of our experiments were performed in the presence of light, which could have led to a low overall observed conversion *cis* \rightarrow *trans*, because the *cis*-isomer is generated from the *trans*-isomer by photochemical isomerization²⁸. In experiments performed in the dark we indeed observed a higher, in many cases complete, *cis* \rightarrow *trans* conversion. Interestingly, the *cis* \rightarrow *trans* isomerization of derivative III proceeded only with 5.4% conversion (Table I).



SCHEME 1

As follows from our results, isomerization via the CT-complex requires higher temperatures (cf. experiments at 25°C and 80°C). Further, it is obvious (Table II) that N,N-diethylaniline forms stronger complexes than aniline, in other words, the former is a better electron donor than the latter. It seems that the presence of sufficiently strong electron accepting groups (such as NO₂, or CO₂CH₃) on substituents in positions 1 and 2 of the ethylene systems represents a rather important condition for formation of the radical anion and for its isomerization. Only in such case the electron transfer along the system, considered in terms of mesomeric structures, can induce the *cis* → *trans* isomerization proper (Scheme 1). The electron, captured e.g. by the NO₂ group, is then transferred through the ethylenic bridge, causing isomerization in this step.

We may conclude that the obtained results correspond with observations on biological systems, using various enzymes as electron donors. Although the ESR spectra showed no radical anion or cation formation in the isomerization reactions of the tight ion pairs, the shifts of UV-maxima indicated that the studied isomerizations do proceed via the CT-complexes.

EXPERIMENTAL

The melting points were determined on a Kofler block and are uncorrected. The ESR spectra were measured on a Bruker ER 200 E — SRC instrument in aniline at 25°C, UV spectra on a Specord UV VIS spectrometer in methanol (λ_{\max} in nm). ¹H NMR spectra were obtained at 28°C with a Varian VXR 300 (300 MHz, FT-mode) instrument in hexadeuterioacetone, using tetramethylsilane as the internal standard, and with a Jeol FX-100 (99.60 MHz) instrument in hexadeuteriodimethyl sulfoxide at 25°C and 70°C. 5-Nitrofurfuryl bromide (*VII*) was prepared from furfuryl alcohol according to ref.²⁹ and 5-nitrofurfuryltriphenylphosphonium bromide (*VIII*) according to ref.³⁰. 4-Nitrobenzyl bromide (*IX*) and 5-methoxycarbonyl-2-furfuryl bromide (*X*) were commercial products. The individual geometric isomers were obtained by fractional crystallization of the mixtures of *E*- and *Z*-isomers from chloroform-hexane (1 : 1). The isomerization reactions were carried out with freshly distilled aniline or N,N-diethylaniline.

4-Nitrobenzyltriphenylphosphonium Bromide (*XI*)

A mixture of bromide *IX* (4.3 g; 0.02 mol), triphenylphosphine (5.3 g; 0.02 mol) and benzene (80 ml) was refluxed for 1 h. The crystals were filtered, washed with benzene and dried to give 7.2 g (76%) of 4-nitrobenzylphosphonium bromide (*XI*), m.p. 269–271°C (reported³¹ m.p. 269–270°C).

5-Methoxycarbonyl-2-furfuryltriphenylphosphonium Bromide (*XII*)

A mixture of bromide *X* (10.9 g; 0.05 mol), triphenylphosphine (13.1 g; 0.05 mol) and benzene (100 ml) was refluxed for 1 h. The separated white material was filtered, crystallized from acetone-methanol and dried. Yield 16 g (67%) of 5-methoxycarbonyl-2-furfuryltriphenylphosphonium bromide (*XII*).

1,2-Bis(5-nitro-2-furyl)ethylene (*I*)

Sodium methoxide solution (from 0.12 g (0.005 mol) of sodium and 2 ml of methanol) and 5-nitro-2-furaldehyde (0.70 g; 0.005 mol) were added at 25°C to a stirred solution of bromide *VIII* (2.33 g; 0.005 mol) in methanol (15 ml). After 5 min, the orange precipitate was collected on filter, washed with methanol and dried; yield 1.15 g (92%) of a 48 : 52 mixture of *E*- and *Z*-isomers, m.p. 186°C (*Z*-isomer; reported³² m.p. 187–189°C) and m.p. 239°C (*E*-isomer; reported³³ m.p. 243–245°C). The isomer ratio was determined by the ¹H NMR spectra. UV spectrum: 208 (3.01), 244 (3.15), 286 (2.97), 412 (3.41), 427i (3.39). ¹H NMR spectrum: (*E*)-*Ia*: 7.31 s, 2 H (H_A, H_B); 7.76 d, 2 H (H-4, *J*(3, 4) = 3.9); 7.17 d, 2 H (H-3). (*Z*)-*Ib*: 6.76 s, 2 H (H_A = H_B); 7.84 d, 2 H (H-4, *J*(3, 4) = 4.2); 7.48 d, 2 H (H-3).

1-(5-Nitro-2-furyl)-2-(4-nitrophenyl)ethylene (*II*)

A) Sodium methoxide (0.54 g; 0.01 mol) was added at 25°C to a stirred solution of phosphonium bromide *XI* (4.78 g; 0.01 mol) and 5-nitro-2-furaldehyde (1.45 g; 0.01 mol) in methanol (50 ml). After 30 min, the yellow precipitate was filtered, washed with methanol and dried; yield, of the ethylene *II* 2.2–2.4 g (85–92%), m.p. 125–127°C (*Z*-isomer) and 179–180°C (*E*-isomer), (reported³⁰ m.p. 179–180°C). The ratio of *E* : *Z* was 64 : 36.

B) Sodium methoxide (0.054 g) was added at 25°C to a stirred solution of phosphonium bromide *VIII* (0.467 g; 0.001 mol) and 4-nitrobenzaldehyde (0.151 g; 0.001 mol) in methanol (6 ml). Already after 1 min the yellow product *II* precipitated (0.15 g; 61%), m.p. 125–127°C (*Z*-isomer) and 175–178°C (*E*-isomer). UV spectrum: 207 (3.08), 231 (3.11), 276 (2.99), 373i (3.27), 384 (3.29). ¹H NMR spectrum (*E*)-*IIa*: 8.311 d, 2 H (H-1, *J*(1, 2) = 8.60); 7.996 d, 2 H (H-2); 7.597 d, 1 H (H_A, *J*(A, B) = 16.50); 7.480 d, 1 H (H_B); 7.608 d, 1 H (H-4, *J*(3, 4) = 3.80); 7.032 d, 1 H (H-3). (*Z*)-*IIb*: 8.302 d, 2 H (H-1, *J*(1, 2) = 8.73); 7.851 d, 2 H (H-2); 7.077 d, 1 H (H_A, *J*(A, B) = 12.70); 6.760 d, 1 H (H_B); 7.483 e, 1 H (H-4, *J*(3, 4) = 3.80); 6.762 d, 1 H (H-3).

1,2-Bis(4-nitrophenyl)ethylene (*III*)

Sodium methoxide (0.054 g) was added at 25°C in the course of 10 min to a stirred solution of phosphonium bromide *XI* (0.47 g; 0.001 mol) and 4-nitrobenzaldehyde (0.15 g; 0.001 mol) in methanol (5 ml). After 2 min, the yellow product *III* precipitated; yield 0.22 g (81%), m.p. 182°C (*Z*-isomer) (reported³⁴ m.p. 183–185°C) and m.p. 287°C (*E*-isomer) (reported³⁵ m.p. 286 to 287°C). The *E* : *Z* ratio was 10 : 90 (for addition of 4-nitrobenzaldehyde to the ylide the ratio was 33 : 67). This mixture was used in the isomerizations at 25°C. UV spectrum: 208 (3.28), 221 (3.21) and 339 (3.22). ¹H NMR spectrum (*E*)-*IIIa*: 7.698 s, 2 H (H_A, H_B); 8.312 d, 4 H (H-1, *J*(1, 2) = 8.90); 7.998 d, 4 H (H-2). (*Z*)-*IIIb*: 7.031 s, 2 H (H_A, H_B); 7.554 d, 4 H (H-1, *J*(1, 2) = 8.80), 8.189 d, 4 H (H-2).

1-(5-Methoxycarbonyl-2-furyl)-2-(4-nitrophenyl)ethylene (*IV*)

A solution of sodium methoxide (0.108 g; 0.002 mol) was added dropwise at 25°C during 5 min to a solution of phosphonium bromide *XII* (0.96 g; 0.002 mol) and 4-nitrobenzaldehyde (0.30 g; 0.002 mol). After 30 min, the yellow precipitate of *IV* was filtered, yield 0.48 g (88%). M.p. 172–180°C (*Z*-isomer) and 183–185°C (*E*-isomer). For C₁₄H₁₁NO₅ (260.3) calculated: 64.54% C, 4.06% H, 5.38% N; found: 64.35% C, 3.96% H, 5.47% N. *E* : *Z* = 75 : 25. ¹H NMR spectrum (*E*)-*IVa*: 3.917 s, 3 H (CH₃); 7.422 s, 2 H (H_A, H_B); 8.284 d, 2 H (H-1, *J*(1, 2) = 8.90); 7.938 d, 2 H (H-2); 6.842 d, 1 H (H-3, *J*(3, 4) = 3.75); 7.310 d, 1 H (H-4). (*Z*)-*IVb*: 3.838 s, 3 H (CH₃); 6.699 d, 1 H (H_A, *J*(A, B) = 12.60); 6.874 d, 1 H (H_B); 8.275 d, 2 H (H-1, *J*(1, 2) = 8.70); 7.830 d, 2 H (H-2); 6.60 d, 1 H (H-3, *J*(3, 4) = 3.65), 7.203 d, 1 H (H-4).

1-(5-Methoxycarbonyl-2-furyl)-2-(5-nitro-2-furyl)ethylene (*V*)

The title compound *V* was prepared in 88% yield as described for *IV*, m.p. 120–124°C (*Z*-isomer) and 168–169°C (*E*-isomer). For $C_{12}H_9NO_6$ (263.2) calculated: 54.71% C, 3.45% H, 5.32% N; found: 54.22% C, 3.53% H, 3.40% N. *E*:*Z* = 71:29. 1H NMR spectrum: (*E*)-*Va*: 3.914 s, 3 H (CH_3); 7.173 d, 1 H (H_A , $J(A, B) = 16.18$); 7.310 d, 1 H (H_B); 7.322 d, 1 H ($H-4'$, $J(3', 4') = 3.69$); 6.940 d, 1 H ($H-3'$); 7.598 d, 1 H ($H-4$, $J(3, 4) = 3.82$); 7.034 d, 1 H ($H-3$). (*Z*)-*Vb*: 3.946 s, 3 H (CH_3); 6.599 d, 1 H (H_A , $J(A, B) = 13.46$); 6.766 d, 1 H (H_B); 7.377 d, 1 H ($H-4'$, $J(3', 4') = 3.69$); 7.295 d, 1 H ($H-3'$); 7.660 d, 1 H ($H-4$, $J(3, 4) = 4.01$); 7.639 d, 1 H ($H-3$).

1-(5-Methoxycarbonyl-2-furyl)-2-(5-nitro-2-thienyl)ethylene (*VI*)

The title compound *VI* was prepared in 95% yield (0.53 g), m. p. 170–180°C (*Z*-isomer) and 194–201°C (*E*-isomer). For $C_{12}H_9NO_5S$ (279.3) calculated: 51.56% C, 3.25% H, 5.01% N; found: 51.02% C, 3.14% H, 5.21% N. *E*:*Z* = 65:35. 1H NMR spectrum: (*E*)-*VIa*: 3.914 s, 3 H (CH_3); 7.282 d, 1 H (H_A , $J(A, B) = 16.14$); 7.449 d, 1 H (H_B); 7.308 d, 1 H ($H-4'$, $J(3', 4') = 3.68$); 6.863 d, 1 H ($H-3'$); 8.022 d, 1 H ($H-4$, $J(3, 4) = 4.40$); 7.455 d, 1 H ($H-3$). (*Z*)-*VIb*: 3.970 s, 3 H (CH_3); 6.673 d, 1 H (H_A , $J(A, B) = 13.08$); 6.861 d, 1 H (H_B); 7.367 d, 1 H ($H-4'$, $J(3', 4') = 3.69$); 6.893 d, 1 H ($H-3'$); 8.027 d, 1 H ($H-4$, $J(3, 4) = 4.35$); 7.594 d, 1 H ($H-3$).

Isomerization of Ethylenes *I*–*VI* in Aniline and *N,N*-Diethylaniline

A) *Isomerization of I at 25°C*. A solution of the mixture of isomeric ethylenes *I* (0.0426 g; 0.2 mmol, *E*:*Z* = 48:52) in aniline (6 ml) was allowed to stand for 165 h, then poured into dilute hydrochloric acid (15 ml of conc. HCl in 40 ml of water), the precipitate was filtered, washed with water and dried, affording 0.0356 g (84%) of 62:38 mixture of *E*- and *Z*-isomers. An analogous reaction was performed at 25°C for 272 h, and at 65°C for 17 h; the obtained mixture of isomers had *E*:*Z* = 90:10.

The same procedure was applied to isomerization of a mixture of ethylenes *II* (*E*:*Z* = 34:66), which after 126 h gave 0.109 g (94%) of a 38:62 mixture of *E*- and *Z*-isomers.

Isomerization of ethylene *III* (*E*:*Z* = 33:67) after 21 h afforded 0.08 g (80%) of a mixture of composition *E*:*Z* = 33:67.

B) *Isomerization of Ethylenes I–VI in Aniline at 80°C*. A mixture of stereoisomeric ethylenes (0.05 g; 0.185 mmol) was dissolved in aniline (20 ml). The obtained deep-red solution of the CT-complex was set aside at 80°C in the dark for 25 h, poured into dilute hydrochloric acid (50 ml of conc. HCl in 100 ml of water) and the separated precipitate was filtered, washed with water and dried.

C) *Isomerization of Ethylenes I–VI in N,N-Diethylaniline*. Products of the isomerization were not isolated and only the UV spectra of their CT-complexes were compared with those of the CT-complex in aniline (see Table II).

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