

## MECHANISM OF ALKENYLATION OF AROMATIC SUBSTRATES WITH 5-NITRO-2-FURYLVINYL BROMIDE

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Mechanism has been studied of electrophilic aromatic substitution with (*Z*)- and (*E*)-5-nitro-2-furylvinyl bromide in the presence of aluminium(III) chloride. From chemical findings and  $^1\text{H}$  NMR study it follows that the mechanism can be interpreted as an electrophilic addition-elimination pathway ( $\text{Ad}_\text{E}-\text{E}$ ) from the point of view of the vinyl substitution.

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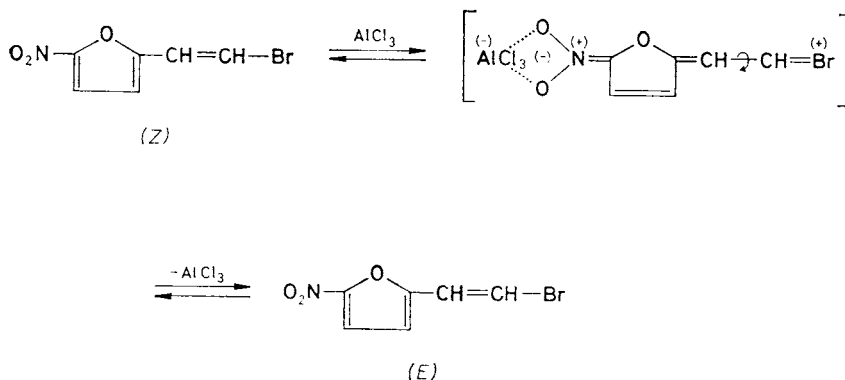
In spite of large number of available experimental data on aromatic alkylations with unsaturated precursors (alkenylations) in the presence of a catalyst, the mechanism of these reaction is only little known. These alkenylations can proceed *via* disubstituted *sp*-hybridized vinyl cations<sup>1</sup>, analogues of acylations and nitrations, or by other processes. A precise mechanistic interpretation of these reactions is difficult due to the complications connected with the heterogeneous catalysts, reaction conditions, the acid present, and possibility of rearrangements.

The aim of the present communication was to elucidate the mechanism of the alkenylation of aromatic compounds under conditions of the Friedel-Crafts reaction with (*Z*)- and (*E*)-5-nitro-2-furylvinyl bromide in the presence of aluminium(III) chloride.

Our previous papers<sup>2-4</sup> dealt with reactions of (*Z*)-5-nitro-2-furylvinyl bromide under the conditions of the Friedel-Crafts reaction with both substituted and unsubstituted aromatic and heteroaromatic compounds in the presence of aluminium(III) chloride. The reactions were carried out in 1,2-dichloroethane at 0°C (the yields with anisole were 28% and 58% at -60°C and 0°C, resp.), above 0°C the reaction mixture contained increasing portions of tarry material. No multiple alkenylation was observed. In all the cases the products isolated were in the thermodynamically stable<sup>5</sup> (*E*)-configuration which is inverted with respect to the starting vinyl halogenide. Besides the reaction products also isolated was an equimolecular mixture of the starting (*Z*)-5-nitro-2-furylvinyl bromide and its (*E*)-isomer formed by isomerization during the reaction. Their structure was confirmed by the  $^1\text{H}$  NMR spectra (Table I).

The isomerization of the starting (*Z*)-vinyl bromide to the (*E*)-isomer during the reaction course can be explained by an attack of the Lewis acid ( $\text{AlCl}_3$ ) on the nitro

group (Scheme 1) which results in possible rotation around the single bond formed in the intermediate complex. This explanation is also supported by the ability of the furane ring to transfer the substituent effects<sup>6</sup>. From literature it is known that the



SCHEME 1

Lewis acids can form complexes with nitro group<sup>7</sup>, nitriles, carboxylic acid esters<sup>8</sup>, etc. An attack of the Lewis acid on the bromide atom or the double bond of ethylene is not excluded, it can take place simultaneously, but the isomerization could not take place in these cases at the reaction conditions given. The <sup>1</sup>H NMR study of a mixture of (Z)-5-nitro-2-furylvinyl bromide and aluminium(III) chloride in 1,2-dichloroethane at 0°C carried out directly in a cell confirmed the (Z-E) isomerization (Table II). The signals corresponding to both the isomers were identified in the spectrum.

The reaction yields depend on reactivity of the aromate and quantity of the catalyst needed for formation of the complex, as it is the case with the Friedel-Crafts acylations<sup>9</sup> (Table III).

The authors<sup>10,11</sup> presume that an electrophilic aromatic substitution with any vinylic compound can proceed by one of the two pathways given in Scheme 2. The mechanism *A* involves the reaction of the proton or Lewis acid and alkylation with the resulting carbenium ion. The mechanism *B* involves the pre-ionization to the intermediate vinyl cation. From the point of view of the nucleophilic vinyl substitution, Rappoport<sup>12</sup> presumes four extreme transition states and intermediates. Two of them involve a reaction *via* carbocation, the other two consider a one- or multi-step course, the nucleophilic attack perpendicular to the double bond being less difficult energetically<sup>13</sup> than the attack in the plane. The occurrence and character of the transition state or intermediate depend on the nucleophile, solvent, and structure of the substrate.

TABLE I

<sup>1</sup>H NMR spectral data of (*Z*)- and (*E*)-isomers of 5-nitro-2-furylvinyl bromide in C<sup>2</sup>HCl<sub>3</sub>, δ(ppm), tetramethylsilane

Isomer	H <sub>3</sub> d	H <sub>4</sub> d	J <sub>3,4</sub> (Hz)	H <sub>A</sub> d	H <sub>B</sub> d	J <sub>A,B</sub> (Hz)
<i>Z</i> <sup>a</sup>	7.29	7.39	4.0	7.12	6.76	8.6
<i>E</i>	6.47	7.29	3.9	7.24	6.92	14.2

<sup>a</sup> According to refs<sup>18,19</sup> the (*Z*)-isomer exhibits *s-cis* conformation ( $J_{A,4}^5 = 0.75$  Hz).

TABLE II

<sup>1</sup>H NMR data of (*Z*)- and (*E*)-isomers of 5-nitro-2-furylvinyl bromide obtained by isomerization of (*Z*)-5-nitro-2-furylvinyl bromide with aluminium(III) chloride in 1,2-dichloroethane, δ(ppm), tetramethylsilane

Isomer	H <sub>3</sub> d	H <sub>4</sub> d	H <sub>A</sub> d	H <sub>B</sub> d
	(J <sub>3,4</sub> (Hz))		(J <sub>A,B</sub> (Hz))	
<i>Z</i>	7.22 (3.8)	7.36 (4.9)	7.09 (8.5)	6.78 (7.3)
<i>E</i>	6.51 (3.8)	7.30 (4.7)	7.19 (13.7)	6.91 (13.7)
<i>Z</i> <sup>a</sup>	7.23 (4.0)	7.35 (5.0)	7.11 (8.5)	6.76 (7.0)

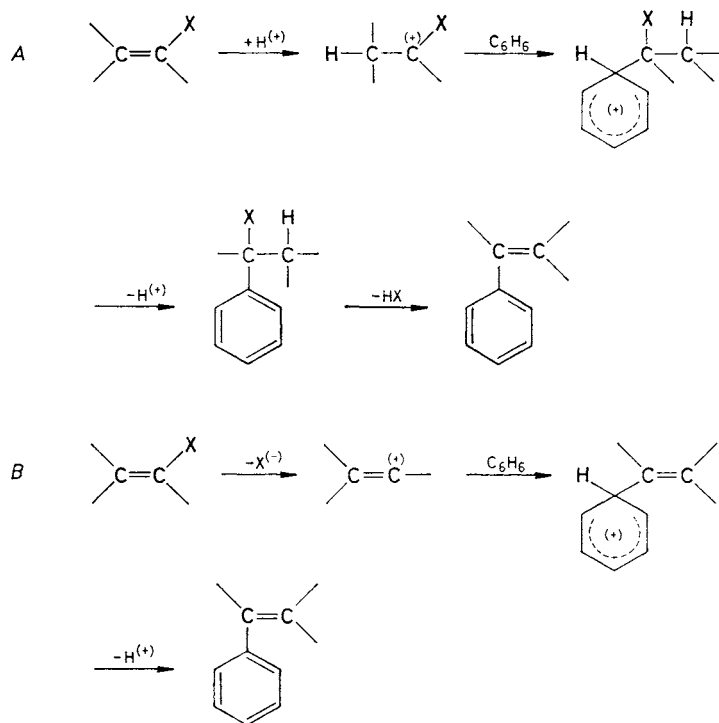
<sup>a</sup> The starting vinyl halogenide in 1,2-dichloroethane before the isomerization.

TABLE III

Dependence of the yield (%) of the reaction of (*Z*)-isomer with anisole and thiophene on the amount of AlCl<sub>3</sub>

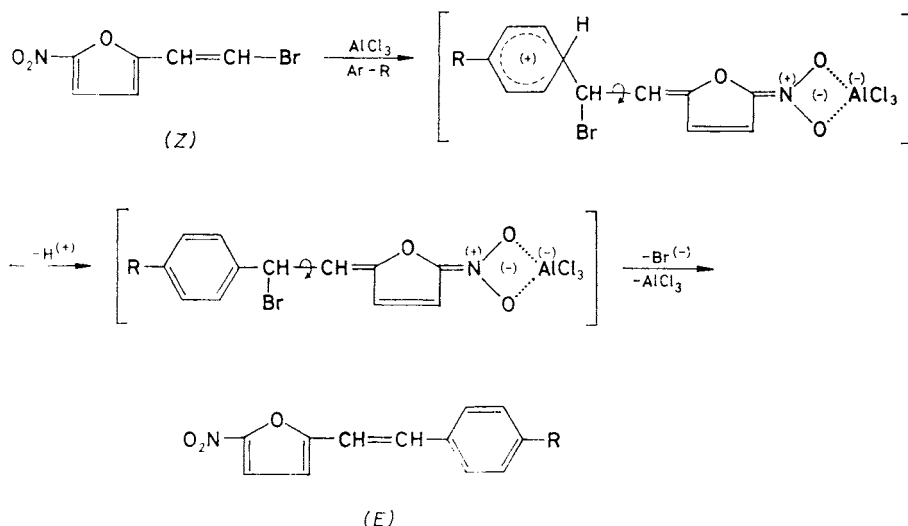
Compound	AlCl <sub>3</sub> , mol		
	0.1	1.0	1.5
C <sub>6</sub> H <sub>5</sub> OCH <sub>3</sub>	5.2	44.1	58.2
C <sub>4</sub> H <sub>4</sub> S	12.0	58.8	67.6

In the reaction studied we preferred the starting (*Z*)-isomer, because it allows to draw significant conclusions about the reaction mechanism from merely inspecting the configuration of the products isolated (retention, inversion, convergency). The



SCHEME 2

(*E*)-isomer, having a higher thermodynamic stability, allows such conclusions to a limited extent only. A study of the reaction mixture composed of the starting (*Z*)-5-nitro-2-furylvinyl bromide, aluminium(III) chloride, and anisole in 1,2-dichloroethane, carried out by means of  $^1\text{H}$  NMR directly in a cell at  $0^\circ\text{C}$  (Fig. 1) indicates formation of the intermediate complex (Scheme 3), because no signals characterizing aromatic and furane protons of the product and no signals due to the protons of the starting (*Z*)- or (*E*)-5-nitro-2-furylvinyl bromide were identified. The proton signals corresponding to the reaction product were not observed even after the reaction time of 30 min. This fact also indicates that the reaction does not proceed *via* the vinyl cation. The formation of the intermediate complex is supported also by the fact that the reaction cannot be realized at enhanced temperatures (ring opening of the dihydrofuran cycle and subsequent formation of tarry materials). The product is isolated after decomposition of the complex with water.



SCHEME 3

From experimental findings and literature data<sup>10,11,14,15</sup> the most probable multistep electrophilic addition-elimination mechanism<sup>12</sup> was suggested ( $Ad_E-E$ , Scheme 3) taking 5-nitro-2-furylvinyl bromide as the substrate. This mechanism allows, after the primary nucleophilic attack, a dispersion of the negative charge localized at the  $\beta$ -carbon atom. In accordance with the theory of variable transition

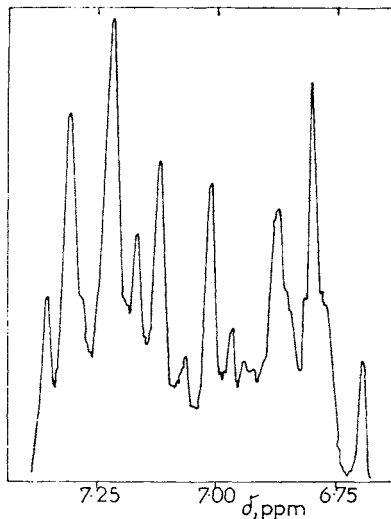


FIG. 1

An  $^1H$  NMR study of a mixture of (*Z*)-5-nitro-2-furylvinyl bromide, aluminium(III) chloride, and anisole in 1,2-dichloroethane at 0°C directly in the cell

state in nucleophilic vinyl substitution<sup>12</sup>, the substitution with the nucleophile represents a multistep process involving the carbanion, if the activating groups exhibit a great ability to delocalize the negative charge.

An analogous reaction of (*E*)-5-nitro-2-furylvinyl bromide with anisole at the same conditions gave an equal yield of (*E*)-2-(4-methoxyphenyl)-1-(5-nitro-2-furyl)-ethylene and an equimolecular mixture of the starting (*E*)-vinyl halogenide and its (*Z*)-isomer.

## EXPERIMENTAL

The starting (*Z*)- and (*E*)-5-nitro-2-furylvinyl bromides were prepared according to refs<sup>16,17</sup>. A general description of the alkenylation is given in our previous papers<sup>2-4</sup>. This method was followed in the reaction of (*E*)-5-nitro-2-furylvinyl bromide with anisole. The yield and physico-chemical data of the product are identical with those in ref.<sup>2</sup>.

The <sup>1</sup>H NMR spectra were measured with a Tesla BS 487 C 80 MHz apparatus in 1,2-dichloroethane at 0°C (1,2-dichloroethane as the internal standard; the chemical shifts were recalculated with respect to tetramethylsilane). The following samples were measured in the corresponding concentrations directly in the cell: (*Z*)-5-nitro-2-furylvinyl bromide in 1,2-dichloroethane, (*Z*)-5-nitro-2-furylvinyl bromide and aluminium(III) chloride in 1,2-dichloroethane, (*Z*)-5-nitro-2-furylvinyl bromide with aluminium(III) chloride and anisole in 1,2-dichloroethane.

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