

## THE COURSE OF REACTION OF 4-NITROBENZYL BROMIDE AND 5-NITROFURFURYL BROMIDE WITH BASES: OPERATION OF ANION-RADICAL MECHANISM

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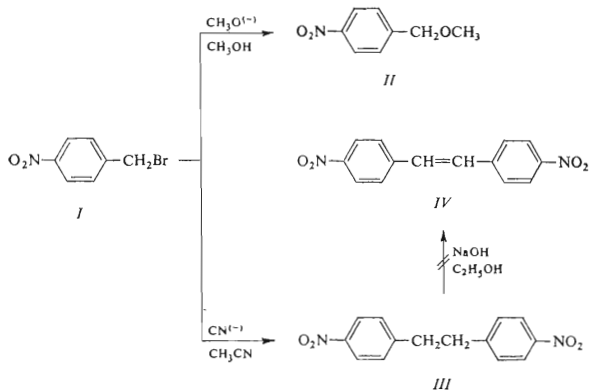
4-Nitrobenzyl bromide (*I*) — contrary to 5-nitrofurfuryl bromide (*V*) — does not react with hard bases in an electron-transfer chain reaction, giving instead product of  $S_N2$  reaction. However, its reaction with soft bases affords 1,2-bis(4-nitrophenyl)ethane (*III*) as anion-radical mechanism product. 5-Nitrofurfuryl bromide reacts with hard bases to give 1,2-bis(5-nitro-2-furyl)ethylene (*VI*) whereas with soft bases 1,2-bis(5-nitro-2-furyl)ethane (*VII*) is formed. The derivative *VII* on reaction with ethanolic NaOH reacts by  $\alpha$ -E<sub>1</sub>cB mechanism under formation of the ethylene derivative *VI*. The derivative *III* does not react by this mechanism. The solvent and base effects on the formation of charge-transfer complexes in the initial stage of these reactions in relation to the reaction mechanism are discussed.

Electron transfer from a donor to a suitable acceptor represents a common feature of chemical as well as biochemical reactions<sup>1</sup>. In the course of reaction, electrostatic interactions of aromatic and heterocyclic nitro derivatives with bases can lead to  $\pi$ -complexes,  $\sigma$ -complexes, charge-transfer complexes or activation of the reacting substrate by a complete electron transfer from the donor (nucleophile) to the acceptor (reacting substrate)<sup>2,3</sup>. A suitable substrate, activated by complete electron transfer, can, according to reaction conditions, further undergo an electron-transfer chain reaction<sup>4-7</sup>. As discussed previously, this mechanism can give rise to various products.

We have found previously<sup>8,9</sup> that 5-nitrofurfuryl derivatives react by  $S_{RN}1$  mechanism under formation of various products, depending on reaction conditions and hardness or softness of the base used. In this communication we compare the reactions of 4-nitrobenzyl bromide (*I*) and 5-nitrofurfuryl bromide (*V*) with hard and soft bases. The reaction of the bromide *I* with various electron donors has already been observed to proceed *via* a radical anion<sup>10-12</sup>.

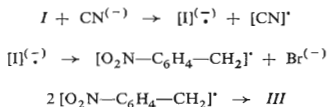
With sodium methoxide in methanol, the bromide *I* affords only the compound *II* (Scheme 1) as product of  $S_N2$  reaction.

On the other hand, the bromide *I* reacts with a soft base ( $CN^-$ ) in acetonitrile to give 1,2-bis(4-nitrophenyl)ethane (*III*), arising by recombination of the 4-nitrobenzyl



SCHEME 1

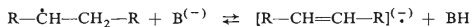
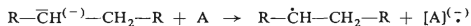
radical formed by anion-radical mechanism (Scheme 2), and no substitution product was detected. Contrary to the analogous nitrofurane derivative, the derivative *III* does not undergo an  $\alpha$ -E<sub>1</sub>cB elimination to give the corresponding ethylenic derivative



SCHEME 2

*IV*. Unlike the bromide *I*, 5-nitrofurfuryl bromide (*V*) reacts with sodium methoxide in methanol by an anion-radical mechanism affording 1,2-bis(5-nitro-2-furyl)ethylene (*VI*) as the principal reaction product whereas the corresponding S<sub>N</sub>2 reaction product is formed in negligible yield (<1%). Also with soft bases (CN<sup>-</sup>), the bromide *V* reacts *via* the radical-anion, the principal product being 1,2-bis(5-nitro-2-furyl)-ethane (*VII*) (Scheme 3).

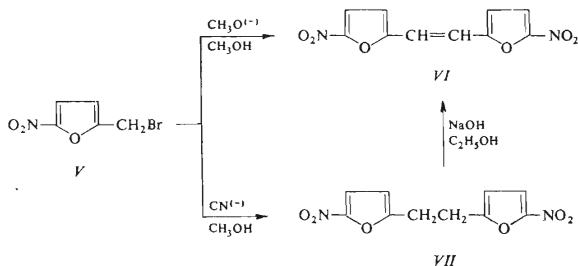
Unlike the compound *III*, the ethane derivative *VII* on reaction with ethanolic sodium hydroxide gives the ethylenic derivative *VI*. The mechanism of this reaction is hitherto not clear. On the basis of the Russell's interpretation<sup>13</sup> we suppose the following general mechanism:



where R = 5-nitro-2-furyl; A = an electron acceptor.

In the first step, similarly to the  $\alpha$ -E<sub>1</sub>cB mechanism, the action of the hard base leads to a carbanion which is further transformed into a radical. In the following steps the end-product is formed *via* the radical-anion. The electron acceptor in this reaction is not known so far and the mechanism is still under study.

The outcome of the reaction of electron transfer-initiated substrate depends on many factors<sup>9,14,15</sup>. Thus, Kornblum<sup>16</sup> has shown that solvent plays a principal role in this reaction. As follows from Scheme 3, the bromide *V* reacts with CN<sup>-</sup> in methanol to give the derivative *VII*. On the other hand, 4-nitrobenzyl bromide (*I*) under the same conditions afforded a mixture of various products, mainly of polymeric nature; however, in acetonitrile or 1,2-dimethoxyethane it gave the ethane derivative *III*. An important factor, influencing the reaction course, are the intensively coloured charge-transfer complexes. The strength of the bond between the electron donor and acceptor (nitro derivative) is obviously decisive for the reaction course. In dimethyl sulfoxide, the bromide *I* and sodium cyanide form a violet complex which hinders further reaction and which after pouring into water liberated the starting bromide *I*. Also 5-nitrofurfuryl nitrate behaves similarly, forming with sodium cyanide in dimethyl sulfoxide a blue charge-transfer complex.



SCHEME 3

The above-mentioned facts show that electron transfer-initiated reactions are influenced decisively by solvating properties of the solvent, the electron accepting power of the substrate and ionisation potential of the electron donor. Generally, it can be stressed that the transfer of electron to the reacting substrate represents a step, decisive for the reaction course. This holds of course also for many other reactions such as those involving an electron transfer from a metal atom to a suitable substrate (Grignard reaction<sup>17-22</sup>, Wurtz reaction *etc.*).

## EXPERIMENTAL

Melting points were determined on a Kofler block and are uncorrected. Thin-layer chromatography was carried out on Silufol UV 254 plates (Kavalier, Czechoslovakia) using benzene as eluant. <sup>1</sup>H NMR spectra were taken on a Tesla BS 487 B instrument (80 MHz) in hexadeuterioacetone at 25°C (internal standard hexamethyldisiloxane). The starting compounds were prepared as follows. Photochemical bromination of 4-nitrotoluene with N-bromosuccinimide in tetrachloromethane afforded 4-nitrobenzyl bromide (*I*). Nitration of furfuryl alcohol with acetyl nitrate in acetic anhydride gave 5-nitrofurfuryl nitrate which on reaction with potassium bromide was transformed into 5-nitrofurfuryl bromide<sup>23</sup> (*V*).

### Methyl 4-Nitrobenzyl Ether (*II*)

The bromide *I* (2.16 g; 0.01 mol) was added at 10°C to a stirred solution of sodium methoxide (from 0.25 g of sodium and 30 ml of methanol). After 1 h the mixture became homogeneous and after 24 h it was taken down. The residue was taken up in ethyl acetate and the crude product was chromatographed on a silica gel (150/250) column with ethyl acetate as eluant. The main fraction afforded 1.62 g (97%) of yellowish crystals, m.p. 26–27°C (reported<sup>24</sup> m.p. 26–27°C). For C<sub>8</sub>H<sub>9</sub>NO<sub>3</sub> (167.2) calculated: 8.38% N; found: 8.42% N. <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 8.18 d, 7.56 d (4 H, aromatic H,  $J_{1,2} = 8.75$  Hz), 4.56 s (2 H, —CH<sub>2</sub>—), 3.40 s (3 H, —OCH<sub>3</sub>).

### 1,2-Bis(4-nitrophenyl)ethane (*III*)

Sodium cyanide (0.5 g; 0.01 mol) was added to a stirred heterogeneous mixture of the bromide *I* (2.16 g; 0.01 mol) and acetonitrile (20 ml). After several minutes, the originally red mixture turned orange. After 6 days the mixture was poured into water (70 ml) and the precipitate was filtered and washed several times with water. After drying, the crude product was chromatographed on a column of silica gel (150/250), using ethyl acetate as eluant. Crystallization of the main fraction from acetone afforded 1.30 g (96%) of yellow product, m.p. 172–173°C (reported<sup>25</sup> m.p. 177.5–179°C). <sup>1</sup>H NMR spectrum,  $\delta$ (ppm): 8.22 d, 7.73 d (8 H, aromatic H,  $J_{1,2} = 8.75$  Hz), 4.74 s (4 H, —CH<sub>2</sub>CH<sub>2</sub>—).

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

5-Nitrofurfuryl bromide (*V*; 2.06 g; 0.01 mol) was added at 20°C to a stirred solution of sodium (0.25 g) in methanol (30 ml). The reaction took place immediately and the solution turned orange. After 10 h the mixture was taken down and the crude product was twice chromatographed on a column of silica gel (150/250), using ethyl acetate and benzene in the first and the second chromatography, respectively. Crystallization from benzene afforded 0.6 g (48%) of the derivative *VI* as orange crystals, melting at 249–250°C (reported<sup>9</sup> m.p. 245°C). The product was identical (thin-layer chromatography) with the authentic specimen of *VI*.

## 1,2-Bis(5-nitro-2-furyl)ethane (VII)

Sodium cyanide (0.5 g; 0.01 mol) was added at 20°C to a stirred solution of the bromide V (2.06g; 0.01 mol) in methanol (40 ml). After 1 h the mixture was taken down and purified by chromatography on a silica gel column (150/250) in benzene as eluant. The derivative VII, obtained in 72% yield, had m.p. 162–164°C (reported<sup>9</sup> m.p. 163°C).

## Reaction of 1,2-Bis(5-nitro-2-furyl)ethane with NaOH

The derivative VII (50 mg) was added at 20°C into a stirred solution of NaOH (100 mg) in ethanol (20 ml). After 24 h the mixture was taken down and the crude product was chromatographed on a column of silica gel (150/250) in ethyl acetate. The orange fraction afforded very low yield of compound VI, m.p. 244–246°C (reported<sup>9</sup> m.p. 245°C).

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