

# Furan derivatives

## CLXXII. S<sub>N</sub> reaction of 5-nitrofurfuryl derivatives with silver or sodium nitrite

<sup>a</sup>I. SROKOVÁ, <sup>b</sup>O. RAJNIAKOVÁ, and <sup>b</sup>A. JURÁŠEK

<sup>a</sup>*Department of Textile, Cellulose and Paper, Slovak Technical University,  
880 37 Bratislava*

<sup>b</sup>*Department of Organic Chemistry, Slovak Technical University,  
880 37 Bratislava*

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The S<sub>N</sub> reaction of 5-nitrofurfuryl derivatives with silver or sodium nitrite leading to 5-nitro-2-furylnitromethane was investigated.

Изучена S<sub>N</sub> реакция 5-нитрофурфуриловых производных с азотистокислым серебром и натрием, ведущая к образованию 5-нитро-2-фурилнитрометана.

Derivatives of nitromethane are frequently prepared by the classic Mayer's method from the corresponding aralkyl halide and silver nitrite, or by the Kornblum's procedure using sodium nitrite [1, 2].

The preparation of 5-nitro-2-furylnitromethane from 5-nitro-2-furfuryl bromide and silver nitrite was described in our paper [2]. 5-Nitro-2-furylnitromethane possesses active hydrogens, which can be utilized in various reactions; therefore, it becomes an important intermediate [2].

This paper deals with further findings encountered with S<sub>N</sub> reactions of 5-nitrofurfuryl derivatives (bromide, iodide, and nitrate) with silver and sodium nitrites.

### Experimental

Infrared spectra of chloroform solutions were measured in a 0.4 mm cell with a UR-20 (Zeiss, Jena) apparatus in the region of 700—3600 cm<sup>-1</sup>; reading accuracy ±1 cm. Electronic absorption spectra of 5 × 10<sup>-5</sup> mol l<sup>-1</sup> solutions in dioxan were recorded with a Specord UV VIS (Zeiss, Jena) spectrophotometer in 1 cm cells in the region of 200—800 nm. The reaction mixture was analyzed with a gas chromatograph—mass spectrometer GC/MS MAT-111 (Varian). For thin-layer chromatography on 20 × 20 cm plates coated with Silica gel LS 5 and gypsum benzene—chloroform 9:1 was used as a solvent system.

## 5-Nitro-2-furylnitromethane

## a) From 5-nitrofurfuryl halide and silver nitrite

An ethereal solution of 5-nitrofurfuryl halide or nitrate (0.1 mol) was added at 0°C or 10°C to a suspension of silver nitrite (0.3 mol) in ether (30 ml) during 1 h; the stirring was continued for 10–30 h. The excess of silver nitrite was filtered off and the filtrate was concentrated under diminished pressure. The results are listed in Table 1.

Table 1

Effect of temperature, reaction time, and the starting material on the yield of 5-nitro-2-furylnitromethane; reaction of 5-nitrofurfuryl derivatives with  $\text{AgNO}_2$

Derivative	Temperature °C	Time h	Yield %
Bromide	0	10	32
Bromide	0	24	44
Bromide	0	30	45
Bromide	10	24	30
Iodide	0	24	28
Nitrate	0	15	0

## b) From 5-nitro-2-furfuryl bromide and sodium nitrite

A cold solution of 5-nitro-2-furfuryl bromide (50 mmol) in dimethylformamide (100 ml) was added with stirring to a heterogeneous solution of  $\text{NaNO}_2$  (5.2 g; 75 mmol) and urea (6 g; 60 mmol) in dimethylformamide (100 ml) cooled to  $-20^\circ\text{C}$ , and the temperature within  $-16$  to  $-18^\circ\text{C}$  was maintained during the next 30 min. The mixture was then poured into an ice-cold water, extracted with ether or benzene, dried over  $\text{Na}_2\text{SO}_4$  and the solvent was removed *in vacuo*. Yield 5.3 g of an oily product, which was analyzed with a gas chromatograph—mass spectrometer. The content of 5-nitro-2-furylnitromethane was estimated by u.v. spectrometry after the product was purified by a preparative thin-layer chromatography. Table 2 lists the results of experiments under varied conditions.

Table 2

Effect of temperature ( $\Theta$ ) and reaction time ( $t$ ) on the yield of 5-nitro-2-furylnitromethane; reaction of 5-nitrofurfuryl bromide with  $\text{NaNO}_2$

$\Theta/^\circ\text{C}$	-12 to -10	-12 to -10	-18 to -20	-23 to -25
$t/\text{h}$	0.5	3.0	0.5	0.5
Yield/%	2.94	2.50	1.98	1.15

## Results and discussion

Conditions of this reaction and the starting substances were varied in order to improve the yield. The results are listed in Table 1. The best results were achieved when using 5-nitro-2-furfuryl bromide and silver nitrite in ether. The optimum temperature and reaction time was 0°C and 30 h, respectively. Further extension of reaction time is of no effect on the yield, which amounts, under the given conditions, 45%. The temperature raise affects unfavourably the purity of the product and the yield (formation of tarry substances). A small amount of 5-nitro-2-furfuryl nitrite, remaining after the removal of 5-nitro-2-furylnitromethane, was attempted to be isolated using both column and thin-layer chromatographies on silica gel, or alumina. Both carriers proved to be unproper and therefore, the residue after crystallization and evaporation of the solvent was distilled under reduced pressure. Only a little amount of a product with boiling point 78—80°C/10.1 kPa was obtained, which exhibited an ONO absorption band in the i.r. spectrum ( $1660\text{ cm}^{-1}$ ). This compound, when left to stand at  $-30^{\circ}\text{C}$  crystallized to a white substance of melting point  $35^{\circ}\text{C}$  lacking the absorption at  $1660\text{ cm}^{-1}$ . This fact indicates that 5-nitro-2-furfuryl nitrite decomposes similarly as its benzene analogue, 4-nitrobenzyl nitrite [3]. 5-Nitro-2-furfuryl bromide was reacted with sodium nitrite in dimethylformamide under the same reaction conditions as with 4-nitrophenylnitromethane [4]. Higher temperatures, e.g. room temperature, and a longer reaction time resulted in formation of an alcohol, nitrite, or furoxane as the main product; the nitro derivative was obtained but in a small amount. Low temperatures led to the same results (cf. Table 2).

The gas chromatographic/mass spectrometric analysis showed this reaction mixture to contain the unreacted 5-nitro-2-furfuryl bromide, 5-nitro-2-furfuryl alcohol and 5-nitro-2-furaldehyde, and an unidentified compound in a 3:2:1:1 ratio. Since 5-nitro-2-furylnitromethane underwent decomposition when analyzed gas-chromatographically, it was determined by u.v. spectrophotometry; calibration curve was constructed with a substance isolated by thin-layer chromatography.

## References

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