THE CONVERSION OF 5-NITROFURFURYL DERIVATIVES INTO 5-AMINOFURFURYLIDENEMALONODINITRILE*

František POVAŽANEC, Jaroslav KOVÁČ and Dušan HESEK
Department of Organic Chemistry,
Slovak Institute of Technology, 880 37 Bratislava

Received December 7th, 1978

The reaction of 5-nitrofurfuryl bromide or 5-nitrofurfuryl iodide with sodium azide and malonodinitrile afforded 5-aminofurfurylidenemalonodinitrile. The intermediate of the reaction is 5-nitrofurfuryl azide which decomposes to give 5-nitrofurfurylideneamine. Its reaction with malonodinitrile gives 5-nitrofurfurylidenemalonodinitrile which reacts further with sodium azide and malonodinitrile to give 5-aminofurfurylidenemalonodinitrile.

We have found previously[1] that 5-nitrofurfuryl nitrate reacts with sodium azide and malonodinitrile, and with methyl cyanoacetate to give, respectively, 5-aminofurfurylidenemalonodinitrile and methyl 3-(5-aminofurfuryl)-2-cyanoacrylate. The amine precursors in this reaction are α-azidofurans[1,2] formed from α-nitro substituted furan derivatives by nucleophilic substitution.

The object of the present work was to explore the course of the reaction with 5-nitrofurfuryl compounds *Ia*–*Id*, to investigate the role of the —CH_2—X group, and to determine whether 5-nitrofurfuryl carbene (*II*) or 5-nitrofurfuryl nitrene (*III*) is the reaction intermediate.

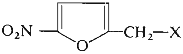
Compounds *Ia*–*Ic* react with sodium azide and malonodinitrile in dimethylformamide or dimethyl sulfoxide to afford 5-aminofurfurylidenemalonodinitrile (*IVa*) and nitrogen (2 mol) is liberated. On the other hand, compound *Id* is unreactive under these conditions and it can be isolated unchanged from the reaction mixture. The liberation of 2 mol of nitrogen together with the observed unreactivity of *Id* indicate that nitrene *III* is the reaction intermediate. When treated with sodium azide in either of the above-mentioned solvents, compounds *Ia* and *Ib* give the azide *Ic*. The latter substance decomposes under acidic conditions and 5-nitrofurfural (*V*) is formed.

Since it can be reasonably assumed that in the reaction under investigation the intermediate azide *Ic* decomposes to *VIa* which can further react with malonodinitrile[3], analogous reactions of azomethines *VIb*–*VIe* have been studied. Compounds

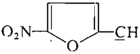
---

* Part CXLV in the series Furan Derivatives; Part CXLIV: This Journal *45*, 746 (1980).

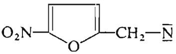
VIb—*VIc* treated with malonodinitrile and sodium azide gave *IVa* in 28% yield. The reaction of malonodinitrile with *VId*—*VIe* afforded 5-nitrofurfurylidenemalonodinitrile (*VIb*) and the corresponding nitroaniline.



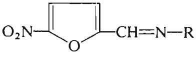
Ia, X = Br
Ib, X = I
Ic, X = N_3
Id, X = SO_2CH_3



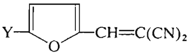
II



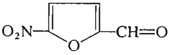
III



VIa, R = H
VIb, R = C_6H_5
VIc, R = 4-CH_3O—C_6H_4
VId, R = 2-$NO_2C_6H_4$
VIe, R = 3-$NO_2C_6H_4$



IVa, Y = NH_2
IVb, Y = NO_2
IVc, Y = N_3



V

Based on the obtained results it can be concluded that the following main stages are involved in the transformation of *Ia* and *Ib*. The first step is the substitution of halogen in *Ia* and *Ib* by the azide ion resulting in the formation of *Ic* which decomposes, with the elimination of nitrogen, to give *III*. A transfer of hydrogen in *III* gives *VIa* which in the presence of malonodinitrile affords *IVb*. Following nucleophilic substitution of the nitro group by the azide ion converts *IVb* into 5-azidofurfurylidenemalonodinitrile (*IVc*). The final step is the conversion of the azido group to an amino group to give rise to *IVc*.

EXPERIMENTAL

The IR and UV spectra were measured with UR-20 (Zeiss) and UV-VIS Specord instruments, respectively. The ^{1}H-NMR spectra (80 MHz) were obtained with a Tesla BS 487 C spectrometer. Melting points were determined on a Kofler hot-stage. The starting materials were prepared as described[4–7].

5-Aminofurfurylidenemalonodinitrile (*IVa*)

A) A mixture of 5-nitrofurfuryl bromide (*Ia*), 5-nitrofurfuryl iodide (*Ib*) or 5-nitrofurfuryl azide (*Ic*) (10 mmol), malonodinitrile (1·3 g; 20 mmol) and sodium azide (1·3 g; 20 mmol) in dimethyl sulfoxide or dimethylformamide (30 ml) was stirred at 30—35°C for 15 min. After further

30 min, the mixture was poured into water and extracted with ethyl acetate. The extract was washed with water, dried, and concentrated under diminished pressure to give *IVa* (0·6 g, 38%), m.p. 198—200°C (ref.[1] 199—200°C). In the case of *Ic* 10 mmol of sodium azide was used. Compound *Ic* (8·5 g, 54%) was prepared[1] from *Ia* or *Ib*, without using HN_3.

B) A mixture of N-(5-nitrofurfurylidene)aniline (*VIb*) or N-(nitrofurfurylidene)-4-methoxyaniline (*VIc*) (10 mmol), malonodinitrile (1·3 g; 20 mmol) and sodium azide (1·3 g; 20 mmol) in dimethyl sulfoxide (30 ml) was stirred at 30°C until the evolution of nitrogen ceased, and worked-up as described in *A*. The obtained crude product was chromatographed on a column of silica gel (acetone–chloroform 1 : 1) to give the amine *IVa* (0·4 g, 28%), m.p. 199—200°C (ref.[1] 199 to 200°C).

Decomposition of 5-Nitrofurfuryl Azide (*Ic*) in Hydrochloric Acid

Concentrated hydrochloric acid (10 ml) was added at 35°C to a mixture of *Ic* (0·5 g, 3 mmol) in ethanol (10 ml). The azide decomposed on heating, and when the evolution of nitrogen ceased the mixture was extracted with ether (100 ml). The ethereal solution was washed with water, aqueous sodium carbonate, dried and concetrated. The residue was fractionated under nitrogen and the fraction that distilled at 130—140°C/2 kPa was collected. The thus obtained compound *V* (0·27 g, 67%) showed m.p. 36°C (ref.[8] 36°C).

5-Nitrofurfurylidenemalonodinitrile (*IVb*)

A mixture of N-(5-nitrofurfurylidene)-2-nitroaniline (*VId*) or N-(5-nitrofurfurylidene)-3-nitroaniline (*VIe*) (2·6 g, 10 mmol) and malonodinitrile (0·7 g, 10 mmol) in dimethyl sulfoxide (15 ml) was stirred at room temperature for 30 min. After addition of water, the precipitated product was filtered and crystallized from ethanol to give *IVb* (1·6 g, 85%), m.p. 174—176°C (ref.[9] 177°C).

REFERENCES

1. Považanec F., Kováč J., Hesek D.: This Journal, in press.
2. Považanec F., Kováč J., Hesek D.: This Journal, in press.
3. Végh D., Kováč J., Dandárová M.: This Journal *41*, 2442 (1976).
4. Jurášek A., Kováč J., Krutošíková A., Hrdina M.: This Journal *37*, 3144 (1972).
5. Hook W. H., Howarth G. H., Hoyle W., Roberts G. P.: Chem. Ind. (London) *18*, 1630 (1955).
6. Takahashi T., Saikachi H.: Yoshima S., Mizuno Ch.: J. Pharm. Soc. Jap. *69*, 284 (1946).
7. Takagi S., Uno T.: J. Pharm. Chem. *20*, 28 (1948).
8. Gilman H., Wright G.: J. Amer. Chem. Soc. *52*, 2552 (1930).
9. Arndt F., Scholz H., Frobel E.: Ann. N. Y. Acad. Sci. *521*, 111 (1935).