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STRUCTURE OF "FURFURAMIDE" AND "FURFURINE"

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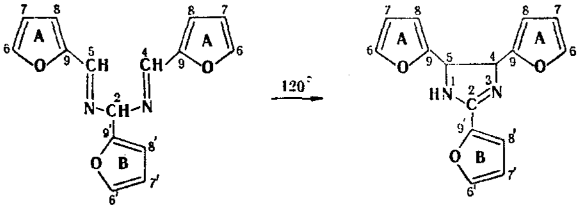
The structures of α,α-bis(furfurylideneimino)silvan ("furfuramide" or N,N'-difurfurylidene-2-furanmethanediamine) and the product of its thermal cyclization 2,4,5-tris(α-furyl)-2-imidazoline ("furfurine") were confirmed by comparison of the IR, UV, ^{1}H and ^{13}C NMR, and mass spectra. It is shown that acetylation of the latter with acetic anhydride in the case of heating of the reagents without a solvent or in pyridine takes place with opening of the imidazoline ring and leads to the formation of 1,2-bis(α-furyl)-1-acetamido-2-(α-furoylamido)ethane.

The extensive application of α,α-bis(furfurylideneimino)silvan ("furfuramide" or N,N-difurfurylidene-2-furanmethanediamine) (I) and 2,4,5-tris(α-furyl)-2-imidazoline ("furfurine") (II) in the production of furan and furan-epoxide resins [1, 2] has recently made it necessary to ascertain and refine their structures. The process for the production of furan and furan-epoxide resins with the use of I presupposes its thermal treatment at temperatures above its melting point (117°C). The aim of the present research was therefore to refine the structures of starting I and its isomer obtained under thermal cyclization conditions:



I II

Structural formula I for "furfuramide" was proposed by Schiff [3]. In 1885 Klaus and Scherbel [4] proposed that the thermal cyclization of I leads to the formation of a compound

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Fergana Division of Furan Compounds, Scientific-Research Institute of Plastics, Fergana 712001. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1461-1464, November, 1978. Original article submitted August 1, 1977; revision submitted December 23, 1977.

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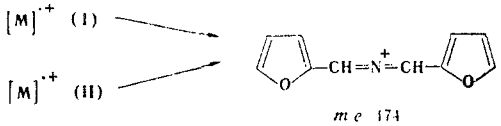
with structure II; however, evidence for this structure was not presented. Moreover, several alternative structures in addition to structure II have existed up until recently [5, 6].

It is apparent from an examination of the UV spectra that two furan rings in I are conjugated with the C═N bond, which leads to an 80-nm bathochromic shift of the maximum of the absorption band of the furan rings as compared with the absorption of furan (maximum at 200 nm [7]). However, in the II molecule only one furan ring is in conjugation with the C═N bond, and the absorption band is shifted only 50 nm to the long-wave region relative to furan.

The mass spectra of these compounds contain molecular ion peaks at 268.* In view of the high symmetry of the molecules the principal fragmentation pathway is that which leads to the formation of the ion at 174, which subsequently undergoes fragmentation with ejection of an HCN molecule and gives an ion at 147; this is confirmed by the presence of a metastable ion at 124 (calculated value 124.2):

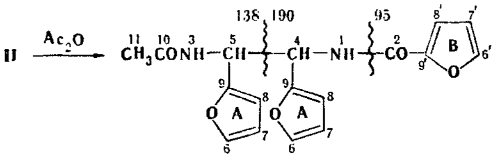


The absence of signals of the protons of the —C═N— fragment in the PMR spectrum of "furfurine" (II) and the appearance of a signal with an integral intensity corresponding to two protons at 5.16 ppm constitute evidence for a change in the character of the hybridization of the 4-C and 5-C atoms from sp^2 to sp^3.† On the other hand, the disapperance of the signal at 6.07 ppm in the spectrum of II as compared with the spectrum of I and the appearance in place of it of a markedly broadened signal with an intensity corresponding to one proton, the chemical shift of which depends on the polarity of the solvent and the temperature, provide evidence for migration of a proton from 2-C to the nitrogen atom. The chemical shifts of the protons of the furan rings undergo characteristic changes. The 6-H, 7-H, and 8-H signals are shifted to high field due to disappearance of conjugation of furan rings A with the C═N bonds, which were present in I but are absent in II.

The development of this sort of conjugation for the B ring in II leads to a shift in the 6'-H, 7'-H, and 8'-H signals to low field. The absolute value of the shift is particularly high in the case of the 8-H and 8'-H protons. As a result, the signals of the 6-H, 7-H, and 8-H protons in the PMR spectrum of II appear in the place of the 6'-H, 7'-H, and 8'-H protons in the spectrum of "furfuramide" and vice versa (see Table 1).

A similar pattern is observed for the 6-C, 7-C, and 8-C signals and the 6'-C, 7'-C, and 8'-C signals in the ^{13}C NMR spectrum, in which one sees a general tendency for a shift of the chemical shifts of these carbon atoms to low field in the case of conjugation of the furan rings with the C═N bond and to high field in the case of disappearance of this conjugation. The signal with doubled intensity at 64.8 ppm corresponds to two sp^3-hydridized 4-C and 5-C atoms of the imidazoline ring of II. In addition to signals of furan rings, only one weak-intensity line (145.6 ppm) of the 2-C atom is present in the region of resonance of sp^2-hybridized carbon atoms.

Finally, the presence of an imidazoline ring in II is confirmed by its behavior during acetylation. It is known that imidazolines are readily converted to acyl derivatives of diamidoethane by acylation [8]. Opening of the imidazoline ring to give 1,2-bis(α-furyl)-1-acetamide-2-(α-furoylamido)ethane (III) also occurs readily in this case by treatment of II with acetic anhydride in the case of gentle heating of the reagents without a solvent or without heating in pyridine:



III

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*Here and subsequently, the m/e values are presented for the ion peaks.

†The equivalence of the 4-H and 5-H protons in II and the form of the signal of these protons in starting I unfortunately make it impossible to discuss their geometry.

TABLE 1. ^1H and ^{13}C NMR Spectra of I-III

Atom No.	^1H NMR			^{13}C NMR		
	I	II	III	I	II	III
1	—	5,37 (at 30°) (s, 1H)	8,40 (m, 1H)	—	—	—
2	6,07 (t, 1H), $J_{2,4,5}=1,3$ Hz	—	—	84,5	145,6	69,5
3	—	—	8,15 (m, 1H)	—	—	—
4 5	8,36 (d, with broadened components, 2H)	5,16 (s, 1H)	5,5 (m, 2H)	150,9	64,8	48,3 48,6
6	7,49 (dd, 2H), $J_{6,7}=1,8$ Hz	7,35 (X portion of an ABX system, 2H),	7,48 (X portion of an ABX system, 2H)	145,3	142,4	141,96
7	6,41 (dd, 2H), $J_{7,8}=0,9$ Hz	6,29	6,25	111,95	106,5	107,05
7^1	6,32	6,43 (dd, 1H), $J_{7,8}=3,5$ Hz	6,46 (dd, 1H), $J_{7,8}=3,5$ Hz	107,8	111,7	111,7
8	6,83 (dd, 2H), $J_{8,6}=0,9$ Hz	6,26 (AB portion of an ABX system 4H), $J_{7,8}=3,1$ Hz $J_{7,6}=1,6$ Hz $J_{8,6}=1,1$ Hz	6,22 (AB portion of an ABX system, 4H $J_{7,8}=3,1$ Hz $J_{7,6}=1,6$ Hz $J_{8,6}=1,1$ Hz	114,9	110,4	110,2
8^1	6,28 (AB portion of an ABX system, 2H), $J_{6',7'}=1,7$ Hz $J_{6',8'}=1,0$ Hz $J_{7',8'}=3,3$ Hz	7,01 (dd, 1H)	6,97 (AB portion of an ABX system, 2H), $J_{6',7'}=1,7$ Hz $J_{6',8'}=1,0$ Hz $J_{7',8'}=3,3$ Hz	110,6	112,7	113,0
9	—	—	—	153,6	154,9	152,8 152,9
9^1	—	—	—	152,3	155,4	147,5
10	—	—	—	—	—	168,6
11	—	—	1,66 (s 1H)	—	—	22,3

The principal pathways of fragmentation of the molecular ion of III under the influence of electron impact are indicated in the schemes.

The IR spectrum of III contains an absorption band at 3340 cm^{-1} corresponding to the vibrations of NH bonds and a strong band at 1670 cm^{-1} corresponding to the vibrations of carbonyl groups.

The PMR spectrum of ethane III differs from the spectrum of imidazoline II in specific details. A singlet at 1.66 ppm (3-H), which is related to the CH_3CO group, appears in the spectrum. The singlet of 4-H and 5-H protons of II is converted in the spectrum of III to a multiplet and is shifted to low field. Two multiplets (8.40 and 8.15 ppm), the integral intensities of which correspond to one proton each, appear at weak field. When the resonance of the 4-H and 5-H protons is suppressed, these signals are converted to singlets. The fact that the character of the spectrum of the protons of the furan rings in II and III is the same in both spectra (i.e., conjugation of the B ring with the π electrons of the sp^2-hybridized carbon atom is retained) makes it possible to assign the structure shown above to III.

The ^{13}C NMR spectrum also confirms the proposed structure of ethane III. In fact, the number of carbon atoms increases by two (from the acetyl group) as compared with II. Disruption of the overall symmetry of the molecule on passing from structure II to III has a pronounced effect on the position of the resonance of the 4-C and 5-C atoms. They become nonequivalent, and, because of the complete absence of conjugation with the furan B ring, the position of their resonance is shifted to 48.3 and 48.6 ppm, respectively. The position of the signals of the carbon atoms of the A rings remain virtually unchanged, but the 9-C atoms become nonequivalent (152.8 and 152.9 ppm). A shift of the signal of this atom to low field (156.95 ppm) is observed because of a change in the character of the conjugation of the 2-C atom with furan ring B, whereas the 9-C atom is shifted correspondingly to high field (147.5 ppm).

EXPERIMENTAL

The PMR and ^{13}C NMR spectra of the compounds were recorded with a WP-60 spectrometer with operating frequencies of 60 MHz (for the PMR spectra) and 15.08 MHz (for the ^{13}C spectra). The parameters of the spectra are presented for solution in $CDCl_3$ with tetramethylsilane as the external standard* and stabilization of the resonance conditions with respect to the deuterium nuclei in the solvent. The assignment of the signals of the proton spectra was accomplished by means of homonuclear double resonance and also by comparison of the spectra recorded with spectrometers with different operating frequencies (WP-60 and HX-90). Selective $\{^{13}C-^{1}H\}$ double resonance was used for the assignment of the lines of the ^{13}C spectra after interpretation of the PMR spectra. A low pulse power (30°) ensured approximate correspondence between the peak size and the number of monotypic atoms at least for the protonated carbon atoms. The IR spectra of KBr pellets and mineral oil suspensions of the compounds were recorded with a UR-10 spectrometer. The UV spectra of solutions of the compounds in alcohol were obtained with an SF-4A spectrophotometer. The mass spectra were recorded with a Varian MAT CH-6 spectrometer with direct introduction of the substances into the ion source.

α,α-Bis(furfurylideneimino)silvan (I). This compound, with mp 117°C, was synthesized by the method in [9] and purified by repeated recrystallization from alcohol. IR spectrum: 1640 (C=N) and 1023 cm^{-1} (C—O—C). UV spectrum: λ_{max} 280 nm (log ε 4.64). Mass spectrum (percent of the maximum ion peak): 268 (6), 239 (0.7), 174 (100), 147 (7), 146 (3), 144 (1.5), 117 (7), 118 (3.4), 106 (3), 94 (6), 93 (4), 91 (9), 81 (9), 80 (5), 79 (4), 78 (14), 67 (7), 53 (8), 52 (15), 51 (12), 39 (14). The ^{1}H and ^{13}C NMR spectra are presented in Table 1. Found: M (by mass spectrometry) 268. $C_{15}H_{12}N_2O_3$. Calculated: M 268.

2,4,5-Tris(α-furyl)-2-imidazoline (II). This compound was obtained by fusion of I at 120°C for 1 h and was purified by repeated recrystallization from alcohol to give a product with bp 250°C and mp 117°C. IR spectrum: 1640 (C=N), 1025 (C—O—C), and 3200 cm^{-1} (NH). UV spectrum: λ_{max} 250 nm (log ε 4.78). Mass spectrum (percent of the maximum ion peak): 268 (5.6), 239 (0.4), 174 (100), 147 (4), 146 (2.4), 119 (2.8), 118 (2.4), 117 (5.2), 95 (4), 94 (4), 91 (5), 81 (5), 80 (5), 79 (3), 78 (7), 65 (4), 53 (5), 52 (15), 51 (8), 39 (12). The ^{1}H and ^{13}C NMR spectra are presented in Table 1. Found: C 67.0; H 4.7; N 10.3%; M (by mass spectrometry) 268. $C_{15}H_{12}N_2O_3$. Calculated: C 67.2; H 4.5; N 10.4%; M 268.

1,2-Bis(α-furyl)-1-acetamido-2-(α-furoylamido)ethane (III). This compound was obtained by treatment of II with acetic anhydride by heating the reagents without a solvent or without heating in pyridine and was purified by repeated recrystallization from alcohol to give a product with mp 250°C (dec.). IR spectrum: 1670 (C=O), 1020 (C—O—C), and 3340 cm^{-1} (NH). UV spectrum: λ_{max} 250 nm (log ε 4.20). Mass spectrum (percent of the maximum ion peak): 190 (45), 155 (3), 139 (6.5), 138 (9), 96 (82), 95 (100), 69 (6.5), 43 (37), 39 (22). The PMR and ^{13}C NMR spectra are presented in Table 1. Found: C 62.5; H 4.9; N 8.8%; M (by cryoscopy) 319. $C_{17}H_{16}N_2O_5$. Calculated: C 62.2; H 4.8; N 8.5%; M 328.

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*The spectra of III were recorded in dimethyl sulfoxide with hexamethyldisiloxane as the internal standard.