# SYNTHESIS BASED ON FURANCARBOXYLIC ACID AMIDES.

## 2.* SYNTHESIS OF DIAMIDES OF THE FURAN SERIES

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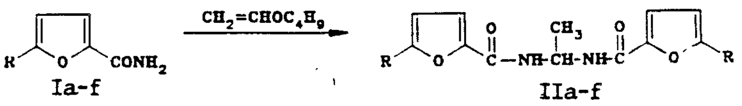
*The corresponding furancarboxylic acid diamides were obtained by the addition of primary amides of furancarboxylic acids to the double bond of vinyl butyl ether and the carbonyl group of various aldehydes..*

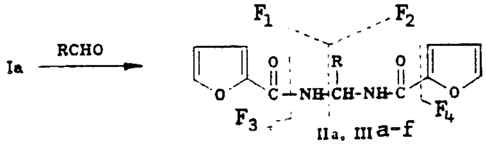
N-Substituted amides of furancarboxylic acids are widely used as pesticides [2, 3], growth regulators [4, 5], and medicinal preparations [6, 7]. Continuing our previous research involving syntheses based on furancarboxylic acid amides, we have carried out reactions involving the addition of the latter to the double bond of vinyl butyl ether and the carbonyl group of various aldehydes.

1,1-Ethylidenebis(5-R-2-furoylamines) IIa-f (Table 1) were obtained by refluxing amides Ia-f with vinyl butyl ether in solution in acetone in the presence of catalytic amounts of hydrochloric acid.



I, II a R=H, b R=CH$_3$, c R=C$_6$H$_5$, d R=Br, e R=I, f R=NO$_2$

Diamides IIa and IIIa-f with various substituents attached to the methylidyne carbon atom (Table 1) were synthesized by the reaction of amide Ia with aldehydes; in contrast to the previously described reaction of some furandicarboxylic acid amides with formaldehyde in solution in toluene in the presence of pyridine [8], we carried out the process in a 3- to 4-fold excess of the corresponding aldehyde in the presence of catalytic amounts of sulfuric acid.



III: a) R = C$_2$H$_5$; b) R = C$_3$H$_7$; c) R = C$_6$H$_5$; d) R = 4-CH$_3$C$_6$H$_4$; e) R = CH = C$_6$H$_5$; f) R = furyl

In the IR spectra of the synthesized compounds (Table 1) one observes the characteristic (for secondary amides) "amide I" and "amide II" bands, stretching vibrations of the NH group, as well as stretching vibrations of the C=C (1575-1620 cm$^{-1}$) and C–H (3130-3180 cm$^{-1}$) bonds of the furan ring. For the crystalline state many of the enumerated bands have the form of either doublets or of one broad band, which is characteristic for compounds of this type [9]. The doublet of the "amide I" band vanishes in spectra recorded in solution in chloroform, and it is shifted 17-25 cm$^{-1}$ to the high-frequency region as compared with the same band for the crystal. The high-frequency "amide II" band in solution is shifted 15-40 cm$^{-1}$ to the low-frequency

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*See [2] for Communication 1.

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TABLE 1. Characteristics of II and III*

| Compound | Empirical formula | mp, °C | PMR spectrum, δ, ppm |  |  |  |  |  | IR spectrum, $cm^{-1}$ |  |  | UV spectrum, $\lambda_{max}$, nm (log ε) | Yield, % |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  | 3-H | 4-H | 5-H | NH | CH | $CH_3$ | "Amide I" | "Amide II" | NH |  |  |
| IIa | $C_{12}H_{12}N_2O_4$ | 173 | 6,98 | 6,48 | 7,58 | 7,95 | 5,97 | 1,53 | 1670, 1655 | 1530, 1565 | 3260 | 253 (4,39), 218 (3,97) | 45 |
| IIb | $C_{14}H_{16}N_2O_4$ | 172 | 6,83 | 6,05 | 2,48 | 7,88 | 5,93 | 1,50 | 1670, 1655 | 1530, 1560 | 3275, 3315 | 270 (4,38), 220 (3,71) | 50 |
| IIc | $C_{24}H_{20}N_2O_4$ | 233 ... 234 | — | — | — | — | — | — | 1685, 1670 | 1520, 1560 | 3275 | 310 (4,20), 231 (4,13), 217 (4,17) | 46 |
| IId | $C_{12}H_{10}Br_2N_2O_4$ | 180 | 6,98 | 6,55 | — | 7,85 | 5,97 | 1,49 | 1670, 1655 | 1530, 1565 | 3255, 3315 | 267 (4,46), 219 (3,89) | 43 |
| IIe | $C_{12}H_{10}I_2N_2O_4$ | 156 | 6,18 | 5,82 | — | 7,87 | 5,59 | 1,50 | 1655 | 1525, 1500 | 3300 | 272 (4,41), 222 (3,86) | 37 |
| IIf | $C_{12}H_{10}N_4O_8$ | 127 | 7,27 | 7,50 | — | 7,85 | 5,99 | 1,48 | 1710 | 1560 | 3400 | 299 (4,30), 218 (4,30) | 50 |
| IIIa | $C_{13}H_{14}N_2O_4$ | 206 ... 207 | 7,13 | 6,60 | 7,73 | 8,41 | 5,73 | 2,53 | 1670, 1655 | 1560, 1525 | 3275, 3100 | 257 (4,33), 219 (3,93) | 59 |
| IIIb | $C_{14}H_{16}N_2O_4$ | 196 | 7,12 | 6,60 | 7,80 | 8,36 | 5,77 | 2,50 | 1670, 1655 | 1560, 1525 | 3285, 3100 | 258 (4,39), 219 (3,91) | 28 |
| IIIc | $C_{17}H_{14}N_2O_4$ | 249 | 7,18 | 6,60 | 7,87 | 8,83 | 6,97 | — | 1670, 1655 | 1530 | 3360, 3320, 3110 | 257 (4,45), 215 (4,03) | 97 |
| IIId | $C_{18}H_{16}N_2O_4$ | 251 ... 252 | 7,13 | 6,60 | 7,85 | 8,75 | 6,93 | — | 1650 | 1530 | 3350, 3330, 3110 | 255 (4,49), 217 (4,20) | 93 |
| IIIe | $C_{19}H_{16}N_2O_4$ | 213 ... 214 | 7,28 | 6,60 | 7,78 | 8,76 | 5,67 | — | 1600 | 1555, 1520 | 3340, 3270, 3070 | 258 (4,14), 215 (4,19) | 33 |
| IIIf | $C_{15}H_{12}N_2O_5$ | 163 ... 165 | 7,17 | 6,58; 6,62 | 7,83 | 8,84 | 7,03 | — | 1685, 1655 | 1545, 1515 | 3335, 3300 | 253 (4,41), 220 (4,11) | 16 |

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*The intensities of the peaks in percent relative to the maximum for the $F_1$, $F_2$, $F_3$, and $F_4$ ions were as follows, respectively: IIa, 100, 0, 100, 38; IIIc, 61, 63, 100, 47; IIIe, 69, 6, 100, 12.

side, whereas the low-frequency band undergoes virtually no change in its position. In the spectrum of a solution one also observes disappearance of the low-frequency band of the stretching vibrations of the NH group; however, a new band of these vibrations appears at 3420-3440 $cm^{-1}$ with a shoulder in the low-frequency region. These data constitute evidence that the molecules of diamides II and III are associated in the crystalline state.

The structures of the synthesized compounds were confirmed by the PMR spectra (Table 1). The PMR spectra contain a multiplet of a methylidyne proton and a doublet of protons of the NH group with a spin-spin coupling constant (SSCC) of 8.3 Hz, which is characteristic for 1,1-diacylaminoethanes [9].

The electronic absorption spectra of diamines II and III (Table 1) are virtually the same as the spectra of starting amides I; this is explained by the presence of identical chromophores in their structures. These spectra contain two absorption bands at 215-222 and 231-299 nm; the long-wave band probably belongs to the $\pi \rightarrow \pi^*$ transition of the basic chromophore, while the other band corresponds to the $\pi \rightarrow \pi^*$ transition in the localized furan ring, which is characteristic for furoyl derivatives [10].

Significant broadening of the low-intensity band is observed in the spectra of IIIc-f; this can be explained by superimposition in the same region of the $\pi \rightarrow \pi^*$ transitions of the electrons in unconjugated phenyl and furoyl radicals.

The mass-spectral fragmentation of the synthesized diamides, which was examined in the case of IIa, IIIc, and IIIe, shows that they are unstable with respect to electron impact. A molecular-ion peak is not observed in the mass spectra of diamides IIa and IIIc, while its relative intensity in the spectrum of IIIe is only 7%. The fragmentation of the molecular ions occurs with the formation of $F_1$ and $F_2$ cation radicals and depends on substituent R. Thus, when $R = CH_3$ (IIa), fragmentation proceeds exclusively with the formation of the $F_1$ cation radical, while the development of both cation radicals is likely when $R = C_6H_5$ or $CH = CHC_6H_5$ (IIIc and IIIe, respectively). The subsequent fragmentation proceeds via the pathway that one usually observes for furan-2-carboxylic acid amides.

## EXPERIMENTAL

The UV spectra of solutions of the compounds in ethanol were recorded with a Specord UV-vis spectrophotometer. The IR spectra of suspensions in mineral oil and in chloroform were obtained with a UR-20 spectrometer. The PMR spectra of solutions in deuteroacetone [IIa-e, hexamethyldisiloxane (HMDS) as the internal standard] and in $d_6$-DMSO (IIIa-f, tert-BuOH as the internal standard referred to HMDS) were recorded with a Tesla BS-467 spectrometer (60 MHz). The mass spectra were obtained with a Varian MAT-112 chromatographic mass spectrometer at an ionizing-electron energy of 70 eV by the method of direct introduction of the samples into the source. The results of elementary analysis of II and III for C, H, and N were in agreement with the calculated values.

**1,1-Ethylidenebis-2-furoylamine (IIa).** A 5.00 g (0.05 mole) sample of vinyl butyl ether and 3 drops of concentrated HCl were added to a solution of 5.55 g (0.05 mole) of furan-2-carboxylic acid amide (Ia) in 40 ml of acetone, and the reaction mixture was refluxed for 1 h. The crystals of IIa that precipitated after cooling of the mixture were removed by filtration and recrystallized from diethyl ether to give 5.58 g (45%) of IIa.

**Compounds IIb-f.** These compounds were similarly synthesized.

**1,1-Propylidenebis-2-furoylamine (IIIa).** Two drops of concentrated $H_2SO_4$ were added to a solution of 2.22 g (0.02 mole) of amide Ia in 10 ml of propionaldehyde, and the mixture was stirred for 1 h. The precipitated crystals were removed by filtration and recrystallized from diethyl ether. This procedure gave 1.56 g (59%) of IIIa.

**Compound IIIb.** This compound was similarly synthesized.

**1,1-Benzylidenebis-2-furoylamine (IIIc).** Two drops of concentrated $H_2SO_4$ were added to a solution of 2.22 g (0.02 mole) of amide Ia in 10 ml of benzaldehyde, and the reaction mixture was heated for 15 min at 40-50°C. The precipitated crystals were removed by filtration and washed with diethyl ether. This procedure gave 3.0 g (97%) of IIIc.

**Compounds IIId-f.** These compounds were similarly synthesized.

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# PHOTOCHEMICAL REACTION OF 7-AMINOCOUMARINS.

## 9.* [2 + 2]-CYCLOADDUCTS WITH trans,trans-1,4-DIPHENYL-1,3-BUTADIENE

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*The photoreactions of 7-diethylaminocoumarin, 4-methyl-7-diethylaminocoumarin, 4-trifluoromethyl-7-diethylaminocoumarin, and 4-N-morpholino-7-diethylaminocoumarin with trans,trans-1,4-diphenyl-1,3-butadiene, which lead to the formation of [2 + 2]-cycloaddition products, were studied. It was established that photocycloaddition proceeds with the formation of adducts that have a 1-endo-styryl substituent and a 2-exo-phenyl group. The effect of the substituent in the 4-position of the 7-aminocoumarin molecule on the effectiveness of cycloaddition is discussed.*

It is known that products of [2 + 2]-cycloaddition at the 3–4 bond that have a phenyl group in the 1-endo-position are formed as a result of the photochemical reaction of 7-aminocoumarins with styrene and trans-stilbene. It has been shown that reactions of this type proceed through the singlet excited state of 7-aminocoumarins and are distinguished by high regioselectivity and stereoselectivity [2, 3].

Since the endo orientation of the 1-phenyl group suggests increased steric requirements in the transition state of cycloaddition, it seemed of interest to ascertain, first of all, how lengthening of the chain of conjugation between the phenyl groups in the olefin affects the stereochemistry of cycloaddition and, second, what effect the substituent in the 4 position of the 7-aminocoumarin molecule has on the effectiveness of the process.

To solve these problems we selected 1,4-trans,trans-diphenyl-1,3-butadiene as the olefin component and, as the substrates, a number of 7-diethylaminocoumarins that have groups with different electronic properties in the 4 position: 7-diethylaminocoumarin (I), 4-methyl-7-diethylaminocoumarin (II), 4-trifluoromethyl-7-diethylaminocoumarin (III), and 4-N-morpholino-7-diethylaminocoumarin (IV).

In all cases only [2 + 2]-cycloadducts V-VIII are formed as a result of the reactions. The actual amounts of V-VIII in the reaction mixtures approach 90-100%; however, as a consequence of a tendency for retrograde decomposition, some of the adduct decomposes during chromatography, and the preparative yields of the cycloadducts range from 60 to 70% (Table 1).

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*See [1] for Communication 8.

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