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ENAMINES OF THE 5-NITROFURAN SERIES

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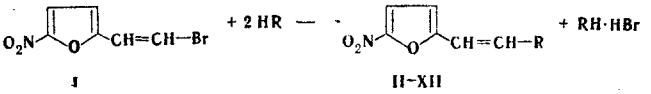
L. V. Nivorozhkin, and J. Kovač

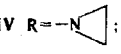
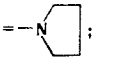
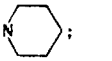
UDC 547.722

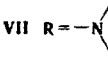
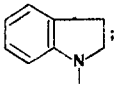
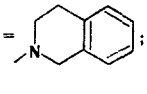
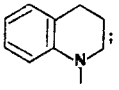
New enamines and quaternary salts of 5-nitro-2-vinylfuran were obtained by reaction of 1-bromo-2-(5'-nitro-2'-furyl)ethylene with secondary and tertiary amines. The trans conformation of the investigated compounds was established by means of their IR, UV, and PMR spectra and dipole moments.

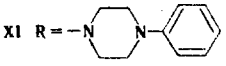
1-Bromo-2-(5'-nitro-2'-furyl)ethylene (I) has recently become an accessible compound [1]. We have investigated its reaction with secondary alkyl- and cycloalkylamines to give intensely colored enamines II-XII:



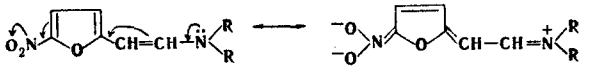
I II-XII

II R = $-N(C_2H_5)_2$; III R = $-N(C_7H_{15})_2$; IV R =  ; V R =  ; VI R =  ;

VII R =  ; VIII R =  ; IX R =  ; X R =  ;

XI R =  ; XII R = $-N(CH_2-C_6H_5)_2$

The reaction proceeds readily at room temperature in anhydrous benzene, acetone, or alcohol, and II-XII are obtained in 50-90% yields (Table 1). The appearance of an intense band of $\pi-\pi^*$ transitions at 490-510 nm in the UV spectra (Table 2) constitutes evidence for the presence of conjugation and a planar structure for the enamines; such a large bathochromic shift of this band as compared with the spectrum of I (342 nm) is evidently associated with the considerable contribution of limiting structure A'', which develops as a result of direct polar conjugation [2]:



A' A''

The planar structures of the II-XII molecules and the presence in them of a high degree of conjugation are also confirmed by the decrease in the $\nu_{C=C}$ band in their spectra to 1620-1630 cm^{-1} (Table 2) [3].

In the synthesis of the enamines we started with the cis isomer of I. However, a study of the PMR spectra showed (Table 3) that in all cases we were able to isolate primarily the trans isomers of the enamines, as evidenced by the spin–spin coupling constants of the H_A and H_B ethylene protons. In the case of II the trans configuration was also confirmed by the good agreement between the dipole moment found experimentally and the value calculated for the

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Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 311-314, March, 1978. Original article submitted January 5, 1977.

 0009-3122/78/1403-0250$07.50

TABLE 1. Enamines of the 5-Nitrofuran Series

Compound	Reaction time, h; temp., °C	mp, °C	R_f	Found, %			Empirical formula	Calculated, %			Yield, %
				C	H	N		C	H	N	
II	30 20—30	63—65	0,18	57,1	6,7	13,3	$C_{10}H_{14}N_2O_3$	57,3	6,8	13,0	90
III	30 20—30	68—71	0,28	68,5	9,8	7,9	$C_{20}H_{31}N_2O_3$	68,7	9,9	7,8	49
IV	100 20—30	71—73	0,13	53,3	4,4	15,5	$C_8H_8N_2O_3$	53,5	4,3	15,2	65
V	100 20—30	86—88	0,07	57,6	5,8	13,4	$C_{10}H_{12}N_2O_3$	57,2	5,9	13,5	80
VI	30 20—30	77—78	0,10	59,4	6,3	12,6	$C_{11}H_{14}N_2O_3$	59,0	6,4	12,8	70—80
VII	30 20—30	129—130	0,16	53,5	5,3	12,5	$C_{16}H_{12}N_2O_4$	53,0	5,5	12,2	80
VIII	50 50—60	150—152	0,18	66,3	5,2	10,3	$C_{15}H_{14}N_2O_3$	66,7	5,4	10,8	75
IX	100 80	103—106	0,46	66,3	5,2	10,3	$C_{15}H_{14}N_2O_3$	66,7	5,3	10,6	55
X	100 80	145—147	0,37	65,6	4,7	10,9	$C_{14}H_{12}N_2O_3$	65,7	4,9	10,6	55
XI	50 20—30	165	0,10	64,2	5,7	14,0	$C_{16}H_{17}N_3O_3$	64,0	5,8	13,9	75
XII	50 20—30	151—152	0,47	71,8	5,4	8,4	$C_{20}H_{18}N_2O_3$	71,9	5,5	8,2	87
XIII	100 110	217—219	0,15*	44,4	3,0	9,4	$C_{11}H_9N_2O_3Br$	43,8	3,2	9,3	65—75
XIV	100 80	278—279	0,06*	51,9	3,2	8,0	$C_{15}H_{13}N_2O_3Br$	51,9	3,4	8,3	65—75
XV	100 70	257—260	0,08*	41,7	4,8	9,9	$C_{10}H_{14}N_2O_3Br$	41,4	4,7	8,1	15—20

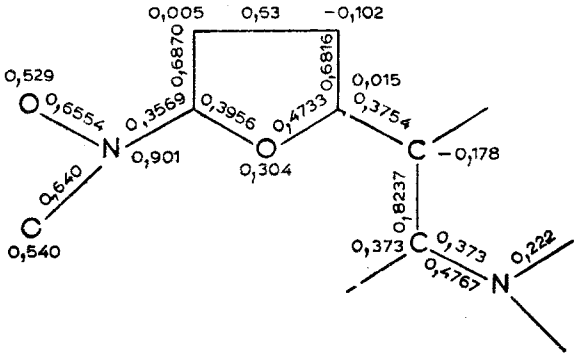
*Ethanol.

trans form (8.729 D, μ_x = 5.133 D, and μ_y = 7.060 D) (Table 3).

In order to predict the reactivities of the synthesized enamines we calculated the π-electron structures, bond orders, and energies of the molecules by means of the Pariser—Parr—Pople (PPP) method within the Dewar $\sigma(\pi_1)$ approximation. The interelectron interaction integrals were calculated from the Mataga—Nishimoto formula, and the resonance integrals were brought into self-consistency with the bond orders from the formula

$$B_{ij}=A_{ij}+B_{ij}\times P_{ij}.$$

By reaction of I with N-heteroaromatic bases (pyridine, quinoline, and isoquinoline)



Molecular diagram of 1-diethylamino-2-(5-nitro-2-furyl)ethylene

and aliphatic tertiary amines we obtained the corresponding stable water-soluble quaternary salts XIII-XV (Table 1):

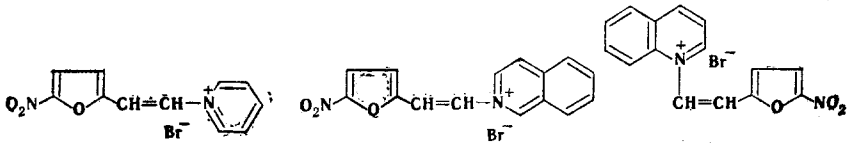


TABLE 2. Electronic and IR Spectra of Enamines II-XV

Compound	UV spectra		IR spectra, cm^{-1}			
	λ_{max}, nm	lg ε	$\nu_{C=C}$	$\nu^{as}_{NO_2}$	$\nu^{s}_{NO_2}$	$\nu_{CH=CH}$
II	280 511	4,26 4,52	1632	1510	1358	955
III	273 509	4,20 4,44	1632	1530	1350	950
IV	270 497	4,30 4,40	1630	1532	1348	954
V	280 510	3,90 4,08	1630	1530	1360	955
VI	280 510	4,41 4,64	1630	1505	1350	948
VII	277 495	4,04 4,20	1633	1505	1350	948
VIII	279 505	4,10 4,19	1635	1530	1350	945
IX	298 313 497	4,45 4,43 4,63	1635	1520	1355	945
X	298 324 508	4,36 4,34 4,47	1645	1525	1340	955
XI	249 277 500	4,35 4,38 4,47	1638	1505	1338	955
XII	278 499	4,23 4,35	1632	1515	1338	958
XIII	225 261 345	4,10 3,80 4,10	1630	1532	1348	962
XIV	218 238 345	4,05 4,02 4,20	1640	1525	1350	962
XV			1635	1535	1350	962

TABLE 3. PMR Spectra and Dipole Moments of Enamines of the 5-Nitrofuran Series

Compound	δ, ppm		$J_{3,4}$, Hz	δ, ppm		J_{AB}, Hz	DM, D
	H_3	H_4		H_A	H_B		
II	6,13	7,26	4	7,35	5,10	14	7,71
VI	6,12	7,38	4	7,27	5,22	14	7,70
VII	6,20	7,41	4	7,28	5,32	14	6,02
VIII	6,21	7,33	4	7,46	5,25	14	7,98
IX	6,28	7,29	4	7,90	5,61	14	6,76
X	6,29	7,27	4	7,92	5,46	14	6,10
XII	6,02	7,25	4	7,70	5,18	14	7,21

A feature common to all of the indicated compounds is the presence in the molecule of a 5-nitro-2-furan fragment, which is responsible for the bactericidal action of compounds of this sort; this enabled us to obtain from them bactericidal preparations with a broad spectrum of activity that have a number of additional valuable properties, information regarding which will be reported separately.

EXPERIMENTAL

The PMR spectra of solutions of the compounds in $(CD_3)_2CO$ were measured with a Tesla PPR spectrometer (60 MHz) with hexamethyldisiloxane as the internal standard. The mass spectra were recorded with an MS-902 apparatus (Jynni AEI). The dipole moments in benzene were determined. The measured concentrations of the solutions ranged from 0.0005 to 0.003 mole fraction. The IR spectra were recorded with a UR-20 spectrometer. The UV spectra of ethanol solutions of the compounds ($5 \cdot 10^{-4}$-$1 \cdot 10^{-5}$ M) were recorded with a Specord UV-vis spectrophotometer. Chromatography was carried out on a loose thin layer of Al_2O_3 (activity II) with elution by benzene–chloroform (1:1).

1-Diethylamino-2-(5'-nitro-2'-furyl)ethylene (II). A 1.46 g (0.02 mole) sample of diethylamine was added to a solution of 2.18 g (0.01 mole) of 1-bromo-2-(5'-nitro-2'-furyl)ethylene (I) in 50 ml of absolute acetone (benzene), and the resulting solution was allowed to stand at room temperature for 1-2 days. The precipitated diethylamine hydrobromide was separated, the filtrate was vacuum evaporated, and the residue was crystallized twice from heptane to give 1.9 g (40%) of red-violet crystals of II with mp 63-65°C.

The characteristics and yields of enamines II-XII are presented in Table 1. In some cases the enamines were purified by reprecipitation from benzene solution by the addition of ether.

1-(5'-Nitro-2'-vinylfuryl)pyridinium Bromide (XIII). A solution of 2.18 g (0.01 mole) of I in 20 ml of pyridine was refluxed for 20 h, after which the excess pyridine was removed in vacuo, and ethanol was added to the residue. The solution was refluxed with activated charcoal, ether was added, and the resulting precipitate was separated to give 2.5 g (85%) of yellow-white crystals with mp 217°C (from alcohol).

Quaternary salts XIV and XV are similarly obtained (Table 1).

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SYNTHESIS OF β-(4,5-DIHALOFURYL)ACRYLIC AND -PROPIOLIC ACIDS

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UDC 547.722.4'725.07

Reaction of 4,5-dihalofurfurals with acetaldehyde and with carbethoxybromomethylenephosphorane gave, respectively, 4,5-dihalofurylacroleins and β-(4,5-dihalo-2-furyl)-α-bromoacrylic acid esters. The latter were converted to 4,5-dihalo-2-furylpropiolic acids by the action of alkali.

It is known that unsaturated furan-2-carboxylic acids have antimicrobial and fungistatic activity [1, 2]. In this connection it seemed of interest to accomplish the synthesis of unsaturated 4,5-dihalofurancarboxylic acids from 4,5-dihalofurfurals. Some β-(4,5-dihalofuryl)-2-acrylic acids have been previously obtained via the Wittig reaction [3]. The synthesis of these acids by condensation of 4,5-dihalofurfurals with acetaldehyde and subsequent oxidation of the resulting furylacroleins to furylacrylic acids seemed to be a promising method.

We established that the reaction of 4,5-dibromo- and 4-bromo-5-iodofurfurals (Ia,b) with acetaldehyde in the presence of sodium hydroxide gives the rather stable 4,5-dibromo-

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Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 315-317, March, 1978. Original article submitted May 31, 1977.

0009-3122/78/1403-0253$07.50